

UNCLASSIFIED

AD NUMBER

AD816588

LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to U.S. Gov't. agencies and their contractors;
Administrative/Operational Use; JUL 1967. Other requests shall be referred to Air Force Rocket Propulsion Lab., Edwards AFB, CA.

AUTHORITY

AFRPL ltr 28 Mar 1974

THIS PAGE IS UNCLASSIFIED

4356

by

July 1967

Sponsored by

1030

"When U.S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, or in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto."

AFRPL-TR-67-200

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER
FOR HIGH ENERGY SOLID PROPELLANTS

by

D. E. Johnson, R. H. Quacchia, and A. J. Di Milo
Aerojet-General Corporation
Solid Rocket Operations
Sacramento, California

This document is subject to special export controls and each transmittal to foreign Governments or foreign nationals may be made only with prior approval of AFRPL (RPPR-STINFO), Edwards, California 93523

W.O. 1030

AFRPL-TR-67-200

FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11419 as partial fulfillment of the requirements of Project 3418 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work reported was done in the Advanced Propellants Department of the Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Corporation Report 1030-81Q-5 and covers the results of work done during the interval 14 March to 13 June 1967. The project was a follow-on to the project completed under Contract AF 04(611)-10386, the results of which are reported in Report No. AFRPL-TR-66-40. Phases One to Three of this program have been completed and the results (including Phase Four results) are reported in AFRPL-TR-67-158. This report reports on Phases Four and Five. This project was monitored by Mr. Robert Corley.

Acknowledgement is made to the following persons who have contributed materially to the work performed during this period: J. L. Humphreys and T. F. Manning, Associate Chemists, F. H. Davidson, Liaison Engineer, Mechanical Properties Laboratories; and at the General Tire and Rubber Company to R. G. Chase, Technical Assistant to the Technical Coordinator, Research and Development.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

This technical report has been reviewed and is approved.

Prepared By:

A J Di Milo

A. J. Di Milo
Program Manager

A J Di Milo
D. E. Johnson *for*
Principal Investigator
Conventional Systems

R H Quacchia
R. H. Quacchia
Principal Investigator
Advanced Systems

Approved By:

MAK for

L. J. Rosen, Manager
Advanced Propellants Department
Research & Technology Operations

ABSTRACT

The acquisition and characterization of hydroxy terminated Telagen S was continued. The functionalities by molecular weight to equivalent weight ratio continue to be below 1.7, but cured binders indicated functionalities in excess of 1.85. The equivalent weights determined by reaction with n-butyl isocyanate were within 2% of values obtained by the manufacturer of the prepolymers. Thin-layer chromatography was used to demonstrate the presence of nonfunctional and monofunctional fractions in Telagen S. Considerable effort was devoted to improving the low temperature properties which may be caused by the high concentration of polar groups in the saturated binder. The use of substitutes for CTI and catalysts studies to achieve room temperature cures were also pursued. PAPI gave good cures with Telagen S, but 1,2,6-hexanetriol has been eliminated as a substitute for CTI. The processing of Telagen S propellants at room temperature is apparently limited more by prepolymer viscosity than by cure rate. Burning rate studies indicate very similar rates for saturated and unsaturated polybutadiene propellants. Cyclic imides have been eliminated as a cure system for advanced oxidizers because of very slow reaction rate with hydroxy groups. The more rapid reacting acid anhydrides have more potential in this area. After two months of aging at 170°F and at relative humidities in excess of 25%, both Telagen S and Minuteman Wing VI Second Stage propellants are degraded.

AFRPL-TR-67-200

TABLE OF CONTENTS

| | <u>Page</u> |
|--------------------------|-------------|
| I. INTRODUCTION | 1 |
| II. OBJECTIVE | 1 |
| III. SUMMARY | 1 |
| IV. TECHNICAL DISCUSSION | 3 |
| A. Prepolymer | 3 |
| 1. Material Acquisition | 3 |
| B. Phase V | 4 |
| 1. Task One | 4 |
| 2. Task Two | 21 |
| 3. Task Three | 26 |
| 4. Task Four | 27 |


TABLES

| <u>Number</u> | | <u>Page</u> |
|---------------|--|-------------|
| I | Properties of Hydroxy Terminated Telagen S | 3 |
| II | Properties of Hydroxy Terminated Telagen S | 4 |
| III | Equivalent Weights of Telagen S by Reaction with C_4H_9NCO | 5 |
| IV | Effect of Prepolymer Equivalent Weights on the Low Temperature Moduli of Binders | 9 |
| V | Effect of Prepolymer Molecular Weights on the Low Temperature Moduli of Propellants | 9 |
| VI | Composition and Properties of Telagen S Binders | 11 |
| VII | Composition and Properties of Telagen S Propellants | 18 |
| VIII | Reaction of Acid Anhydrides with 2-Octanol in the Presence of HAP at Room Temperature | 24 |
| IX | Reaction of Various Cyclic Imides with 1-Octanol in the Presence of HAP at 50°C | 26 |
| X | Catalysis of the Reaction of N-Butyl Isocyanate (0.2N) with Prepolymer 148AH (0.2N) in Toluene at Room Temperature | 31 |
| XI | Aging Conditions | 32 |
| XII | Mechanical Behavior of Telagen S and Minuteman Wing VI Second Stage Propellants at -75°F and 100% Relative Humidity in Carbon Dioxide Environment | 33 |
| XIII | Mechanical Properties of Telagen S and Minuteman Wing VI Second Stage Propellants at 0°F and 100% Relative Humidity in Carbon Dioxide Environment | 34 |
| XIV | Mechanical Properties of Telagen S and Minuteman Wing VI Second Stage Propellants at 77°F and 5% Relative Humidity in Stagnant Nitrogen Environment | 35 |
| XV | Mechanical Properties of Telagen S and Minuteman Wing VI Second Stage Propellants at 77°F and 50% Relative Humidity in Stagnant Nitrogen Environment | 36 |

TABLE OF CONTENTS (Cont)

| <u>Number</u> | | <u>Page</u> |
|---------------|---|-------------|
| XVI | Mechanical Properties of Telagen S and Minuteman Wing VI Second Stage Propellants at 77°F and 25% Relative Humidity in Circulating Air Environment | 37 |
| XVII | Mechanical Properties of Telagen S and Minuteman Wing VI Second Stage Propellants at 77°F and 50% Relative Humidity in Circulating Air Environment | 38 |
| XVIII | Mechanical Properties of Telagen S and Minuteman Wing VI Second Stage Propellants at 77°F and 80% Relative Humidity in Stagnant Air Environment | 39 |
| XIX | Mechanical Properties of Telagen S and Minuteman Wing VI Second Stage Propellants at 170°F and 25% Relative Humidity in Circulating Air Environment | 40 |
| XX | Mechanical Properties of Telagen S and Minuteman Wing VI Second Stage Propellants at 170°F and 80% Relative Humidity in Stagnant Air Environment | 41 |

FIGURES

| <u>Number</u> | | <u>Page</u> |
|---------------|--|-------------|
| 1 | Gel Fractions of Binders Prepared with Varying Prepolymer, Lot 158H, CTI Ratios | 6 |
| 2 | Thin-Layer Chromatogram of Carboxy-Terminated Telagen S | 8 |
| 3 | Gel Fractions of Unsaturated Telagen S (Lot 148A) Binders with Varying Equivalent Ratios of CTI to Total Isocyanate | 14 |
| 4 | Gel Fractions of Telagen S Binders with Varying Amounts of CTI | 16 |
| 5 | Pressure-Burning Rate Relation for Saturated and Unsaturated Polybutadiene Propellants | 22 |
| 6 | Chromatogram of Acetic Anhydride - 2-Octanol in Benzene | 23 |
| 7 | Gas-Liquid Chromatogram of 1-Octanol, Hexahydrophthalimide, and Phenylcyclohexane in Benzene | 25 |
| 8 | Infrared Spectrum of $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{COOCH}_3)_2$ | 28 |
| 9 | Infrared Spectrum of $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{COOCH}_3)_2$ | 29 |
| 10 | Infrared Spectrum of  $\text{NCH}_2\text{CH}_2\text{COOCH}_3$ | 30 |
| 11 | Maximum and Break Elongations for Propellants Aged in Circulating Air, 25% Humidity and 170°F | 43 |
| 12 | Maximum and Break Elongations for Propellants Aged in Stagnant Air, 80% Humidity and 170°F | 44 |
| 13 | Maximum Tensile Stress and Initial Moduli for Propellants Aged in Circulating Air, 25% Humidity and 170°F | 45 |
| 14 | Maximum Tensile Stress and Initial Modulus for Propellants Aged in Stagnant Air, 80% Humidity and 170°F | 46 |

GLOSSARY

| | |
|--------------------|--|
| Ansul Ether 181 | Tetraethylene glycol dimethyl ether |
| AR | Burning rate modifier, Aerojet-General proprietary compound |
| C_1 and C_2 | Mooney-Rivlin Constants |
| CoAA | Cobalt acetylacetonate |
| CTI | Triisocyanate, proprietary item of the Aerojet-General Corporation |
| DOS | Diethyl sebacate, product of the Deecy Products Division, Reichold Chemicals, Inc. |
| E_0 | Initial uniaxial modulus |
| FeAA | Ferric acetylacetonate |
| GTRO | Glycerol triricinoleate |
| HAA | Acetylacetone |
| HDI | Hexamethylene diisocyanate |
| IDP | Isodecyl Pelargonate, product of Emery Industries, Inc. |
| kg/cm^2 | Kilograms per square centimeter |
| meq/gm | Milliequivalents per gram |
| Methyl Nadic Imide | Imide of methylbicyclohepta-5-ene-2,3-dicarboxylic acid |
| mm/gm | Millimoles per gram |
| Nacconate H-12 | Bis(4-isocyanatocyclohexyl)methane, product of the Allied Chemical Corporation |
| Niax D-22 | Dibutyltin dilaurate, product of the Union Carbide Co. |
| PAPI | Polyphenyl polyisocyanate, product of the CPR Division, Upjohn Company |
| psi | Pounds per square inch |

GLOSSARY (Cont)

| | |
|---------------|--|
| T-18 | Stannous type catalyst, product of Metal & Thermit Corp. |
| Telagen S | Functionally-terminated hydrogenated polybutadiene, product of The General Tire and Rubber Company |
| TDI | 2,4-Toluene diisocyanate |
| Thermalite 25 | Complex organotin compound, product of Metal & Thermit Corp. |
| v_2 | Gel fraction |
| VPO | Vapor phase osmometer |
| ϵ_b | Uniaxial strain at break |
| ϵ_m | Maximum uniaxial strain |
| σ_b | Uniaxial break stress |
| σ_m | Uniaxial maximum stress |

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER
FOR HIGH ENERGY SOLID PROPELLANTS

I. INTRODUCTION

This is the fifth Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11419. The report covers the period 14 March through 13 June 1967.

II. OBJECTIVE

The objective of this program is to further develop and evaluate a solid propellant binder system specifically to meet the most rigid demands of advanced, high performance solid rocket motors. The solid propellant binder system consists of an isocyanate-cured, saturated hydrocarbon prepolymer developed and evaluated under Contract AF 04(611)-10386. Further development and evaluation will involve propellant optimization, testing of curatives for room temperature cures, replacing CTI, attaining better low temperature properties, determining the effect of burning rate modifiers, adaptation to advanced fuels and oxidizers, formulations containing both advanced fuels and oxidizers, and a study of environmental stability.

III. SUMMARY

A. Both a secondary and primary hydroxy terminated Telagen S have been received and characterized. The secondary hydroxy prepolymer, Lot 242AM-161AHR, has a functionality (MW:EW) of 1.49 and an actual functionality less than that of Lot 148AH and very similar to that of 158H. The primary hydroxy prepolymer, Lot 242AM-168H, has a functionality (MW:EW) of 1.63 and an actual functionality higher than that of 161AHR.

B. The equivalent weights of the prepolymers determined at Aerojet check within 2% of values determined at The General Tire and Rubber Company. The Aerojet determination involves reaction of the prepolymer with n-butyl isocyanate.

C. While Prepolymer 148AH cured more rapidly than either 158H or 161AHR, the amounts of isocyanate consumed by all three polymers in 18 hours were very similar. This leads to the conclusion that the faster cure rate of Prepolymer 148AH is due to a shorter gel time resulting from a higher functionality.

D. Hydroxy and carboxy terminated Telagen S were fractionated by thin-layer chromatography by silica gel on glass fibers. Non-acidic, moderately acidic, and strongly acidic fractions were obtained from the carboxy terminated prepolymer.

E. Since the low temperature behavior of Telagen S binders may be determined by the high carbamate content, low molecular weight diols have been added to Telagen S to further increase the carbamate content of binders and to determine its effect on the low temperature behavior. The first attempt with 1,4-dimethylolcyclohexane was not successful because the cyclohexane derivative was not compatible with Telagen S. While octanediol and decanediol were also incompatible, hexanediol and pentanediol were compatible. Mechanical data are not yet available.

F. PAPI and 1,2,6-hexanetriol have been used as replacements for CTI in Telagen S binders and propellants. While PAPI looks promising and is being investigated further, the hexanetriol shows no promise as a replacement for CTI. Glycerol triricinoleate is also being tried as a replacement for CTI.

G. Studies indicate that FeAA and Niax D-22 are active enough catalysts to cure Telagen S propellants at room temperature, but propellant studies show that the viscosity of the prepolymer affects the castability of the propellant and becomes the limiting factor in low temperature ($< 110^{\circ}\text{F}$) processing.

H. Propellant studies have continued to verify and expand the results of binder studies. The best cure stoichiometry for propellants seems to be an NCO to OH ratio of 1.02 although the cure time is increased at this ratio.

I. Burning rates of propellants with saturated and unsaturated prepolymers are very similar. The pressure exponent increases from 0.4 to 0.9 between 600 and 1000 psia.

J. Acid anhydrides were shown to react rapidly and stoichiometrically with hydroxy functional groups in the presence of HAP. The reaction rate was slowest with the phthalic anhydride and the potential of this type of agent for curing HAP propellants is being pursued.

K. Cyclic imides were investigated as potential curing agents for HAP. Their rate of reaction with hydroxyl groups was very slow and was not catalyzed by HAP. This curing system has been abandoned because no method of increasing the reaction rate was available.

L. The synthesis of an azetidine (4-membered, nitrogen-containing ring system) derivative was initiated. The material will be investigated as a curing system for advanced oxidizers. Azetidines should be less prone to side reactions than aziridines.

M. After two months of aging, both Telagen S and Minuteman Wing VI Second Stage propellants show no degradation at -75°F , 0°F , and 77°F . At 170°F both types degraded seriously, especially under the influence of humidity.

IV. TECHNICAL DISCUSSION

A. PREPOLYMER

1. Material Acquisition

A batch of hydroxy terminated Telagen S requested for use in Phase IV of this program was delivered and evaluated. The properties of the material (Lot 242AM-161AHR) are shown in Table I.

Table I

PROPERTIES OF HYDROXY TERMINATED TELAGEN S
(Lot 242AM-161AHR)

| | |
|--------------------------------------|-------|
| Molecular Weight (VPO) | 1670 |
| Hydroxyl Content, meq/g | 0.895 |
| Equivalent Weight | 1117 |
| Functionality ^a | 1.49 |
| Unsaturation, mm/g | 0.4 |
| Brookfield Viscosity, poises at 25°C | 132 |
| Water Content, % | 0.01 |
| Volatiles, % | 0.4 |
| Sulfated Ash, % | 0.04 |
| Antioxidant, % | 0.36 |

^aMolecular weight/equivalent weight

Another batch of hydroxy (primary) terminated Telagen S, requested for use in Phase V of this program, was received and is being evaluated for a room temperature cured propellant. The primary hydroxyl groups will increase the rate of the cure reaction at lower temperatures. The properties of the material (Lot No. 242AM-168H) are shown in Table II.

Table II

PROPERTIES OF HYDROXY TERMINATED TELAGEN S
(Lot No. 242AM-168H)

| | |
|--------------------------------------|-------|
| Molecular Weight (VPO) | 1800 |
| Hydroxyl Content, meq/gm | 0.904 |
| Equivalent Weight | 1108 |
| Functionality ^a | 1.63 |
| Unsaturation, mm/gm | 1.30 |
| Brookfield Viscosity, poises at 25°C | 159 |
| Water Content, % | 0.01 |
| Volatiles, % | 0.14 |
| Sulfated Ash, % | 0.07 |
| Antioxidant, % | 0.20 |

^aMolecular weight/equivalent weight

The equivalent weight, determined by reaction with n-butyl isocyanate, was 1080.

B. PHASE V

1. Task One

a. Introduction

Task One will involve prepolymer characterization, improved low temperature properties, curing agent substitutes for CTI, the effects of plasticizer and burning rate modifiers, room temperature curing and boron-workhorse binder systems. A propellant designed for low temperature capability, a propellant cured at room temperature, and a propellant with a CTI replacement will be prepared for long-term aging.

b. Prepolymer Characterization

1) Equivalent Weights of Prepolymers

The equivalent weights of some prepolymers were

examined using two methods. One involves varying the ratios of isocyanate (CTI) to prepolymers and the other method, used successfully by Dr. A.E. Oberth, involves the reaction of the prepolymer with butyl isocyanate.

The prepolymer 158H was cured with various ratios of prepolymer to CTI, (Figure 1). From the variation of the gel fractions with the prepolymer to CTI ratios, the equivalent weight of Prepolymer 158H was deduced to be slightly higher than 1130. Two binders, Nos. 139 and 140, Table IV, were prepared using 1190 as the equivalent weight and these were found to be softer than Nos. 133 and 134 which were based on an equivalent weight of 1132. This confirmed the vendor's equivalent weight of 1130.

While the above method is practical for determining equivalent weights under reaction conditions, the method is time consuming and not as accurate as other methods. Equivalent weights were obtained by reacting the polymer overnight with excess n-butyl isocyanate in toluene at room temperature and then determining the unreacted isocyanate. Controls were run to correct for isocyanate disappearance through side reactions. The data for various prepolymers are shown in Table III.

Table III

EQUIVALENT WEIGHTS OF TELAGEN S BY REACTION WITH C_4H_9NCO

| <u>Prepolymer Lot No.</u> | <u>Equivalent Weight</u> | |
|---------------------------|--------------------------|--------------------------------------|
| | <u>Vendor</u> | <u>C_4H_9NCO Method</u> |
| I-47.1 | 980 | 960 |
| 148AH | 1100 | 1075 |
| 158H | 1130 | 1110 |
| 161AHR | 1120 | 1110 |
| 161AHR | 1120 | 1115 |
| 168H | 1108 | 1080 |

Although all of the equivalent weights were slightly lower, the values are within 2% of the vendor analyses.

2) Cure Rate

During the preparation of binders, it was observed that prepolymer 148AH promoted faster cures than did other prepolymers. To

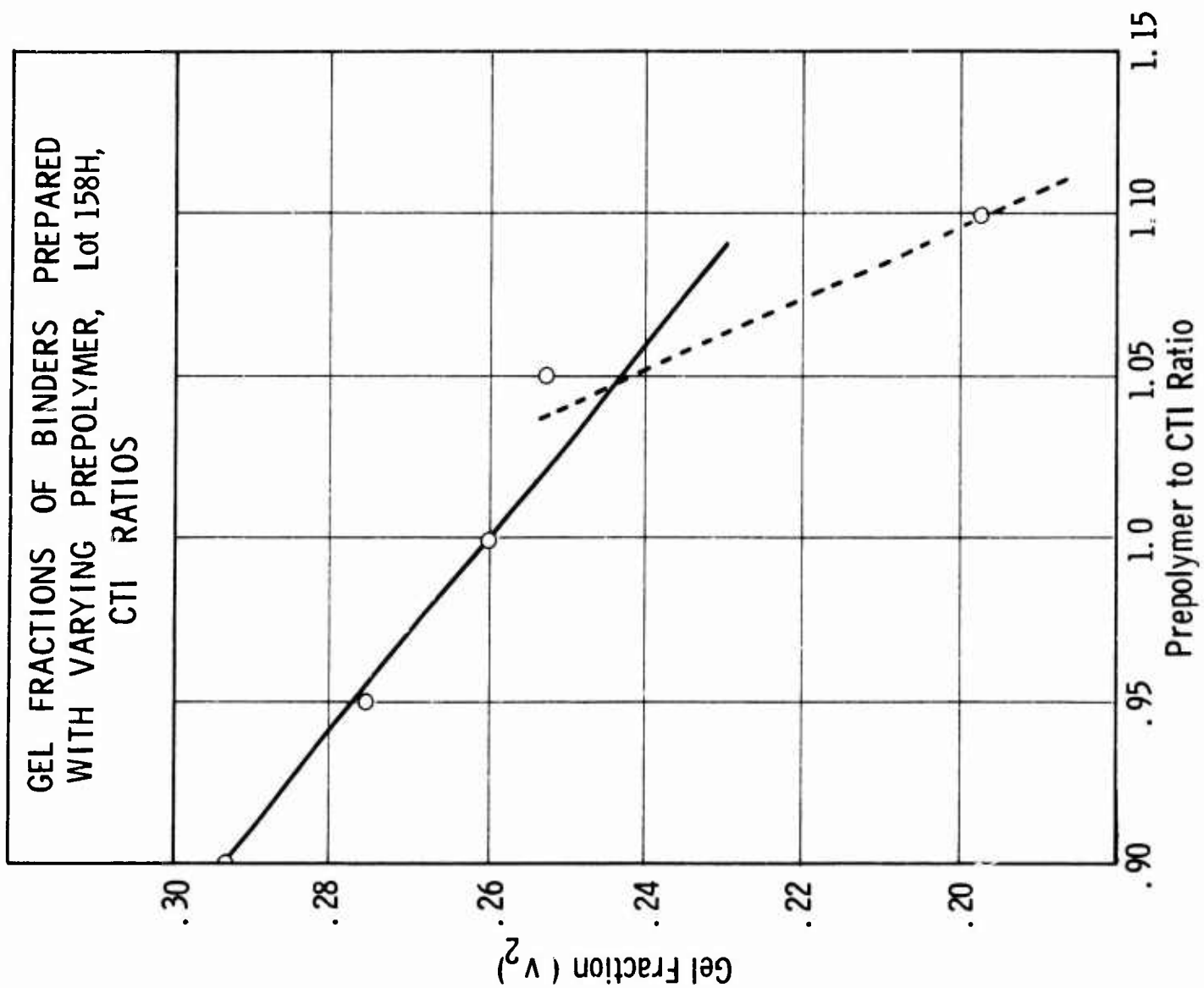


Figure 1



test this observation, 0.2N solutions of various prepolymers and phenyl isocyanate were made in toluene and the ensuing reaction was followed at room temperature by analysis for unreacted isocyanate. In 18 hours, 28.3% of the isocyanate remained in the solution containing Prepolymer 148AH. With Prepolymer 158H, 29.8% isocyanate remained and with Prepolymer 161AHR, 30.8% remained under the same conditions. These differences are not significant, however, a precipitate developed in 148AH and 158H which was identified as s-diphenylurea (carbanilide).

n-Butyl isocyanate was used in similar experiments and the results were similar except that this isocyanate reacted about 20 times slower. Definite color changes were observed during the first 3 days of these runs. The solution containing prepolymer 148AH became deep red-orange; 158H, a dark orange; and 161AHR remained straw colored.

The conclusion is that Prepolymer 148AH does not react more rapidly. The faster cure rate is the result of the higher functionality of 148AH which causes a shortening of the gel time. More definitive studies are in progress.

3) Prepolymer Chromatography

Gel determinations done under the present program and the functionality studies done by Esso Research and Engineering Company⁽¹⁾, indicate a significant amount of non- and/or monofunctional materials in these prepolymers. Both carboxy- and hydroxy-terminated prepolymers were fractionated by thin layer chromatography using basic silica gel on glass fibers. n-Hexane was used initially as the developing solvent and iodine as the indicator. The composition of these fractions was not determined.

Further work was done with the carboxy-terminated prepolymer, 148DH3, because bromcresol green could be used as an indicator for the functional groups. With ethyl acetate a non-acidic fraction (brown in presence of I_2 ; not affected by bromcresol green) was separated from the acidic fraction (Figure 2). A mixed benzene, ethanol, glacial acetic acid (90:16:4) solvent further separated the acid fraction into two fractions one of which, because of lower response to bromcresol green, was judged less acidic than the other which was not moved on the paper. It is possible that the less acidic material may be monofunctional but this is conjecture. Quantitative estimates of the amounts of each fraction could not be made. The technique is a rapid method of characterizing prepolymers, and it may, possibly, be developed as a semiquantitative method. Emphasis on other phases of this program has temporarily halted the work in this area.

c. Low Temperature Properties

The low temperature capabilities of Telagen S propellants have been marginal up to the present time. Most recent evidence indicates

THIN-LAYER CHROMATOGRAM OF CARBOXY-TERMINATED TELAGEN S (Lot 148 DH3)

Solvent: Benzene-Ethanol-Acetic Acid (90:16:4) Solvent: Ethyl Acetate

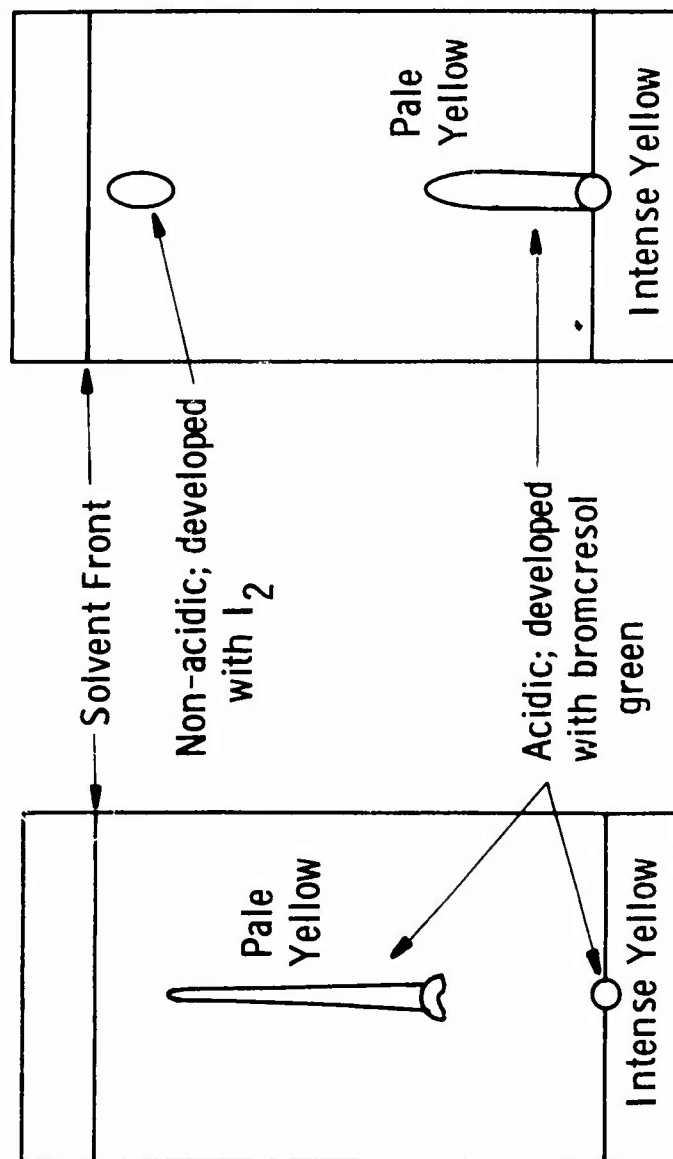


Figure 2

that motor grains of Telagen S propellants can be cycled to -40°F without cracking⁽²⁾⁽³⁾. An improvement of this capability is being sought.

Previous work⁽²⁾⁽⁴⁾ has indicated that crystallization of the prepolymer or binder is not a cause of the low temperature limitations. It is postulated that the high concentration of urethane groups caused by the use of a low molecular weight prepolymer is setting a limit on the low temperature properties. This effect is illustrated by the data for unsaturated prepolymers (Tables IV and V) which were obtained by Dr. Oberth and H. Michigian on Aerojet-General sponsored programs. The main effort is being devoted to substantiating this hypothesis for Telagen S.

Table IV

EFFECT OF PREPOLYMER^a EQUIVALENT WEIGHTS ON THE
LOW TEMPERATURE MODULI OF BINDERS

| Prepolymer Equiv. Wt. | Initial Modulus, psi, at | | |
|--------------------------|--------------------------|-------|-------|
| | 77°F | -40°F | -75°F |
| 3100 | 60 | 250 | 280 |
| 2833 | 15 | 60 | 110 |
| 2700 | 28 | 80 | 120 |
| 2400 | 84 | 250 | 270 |
| 1038 | 19 | 190 | 3950 |

^aUnsaturated, hydroxy terminated polybutadienes

Table V

EFFECT OF PREPOLYMER^a MOLECULAR WEIGHTS ON THE
LOW TEMPERATURE MODULI OF PROPELLANTS

| Prepolymer Molecular Wt. | Propellant Modulus at -75°F, psi |
|-----------------------------|-------------------------------------|
| 2000 | 11000 |
| 5000 | 8800 |

^aUnsaturated, hydroxy terminated polybutadienes

For this purpose, a series of prepolymers of molecular weights ranging from 1000 to 4000 has been ordered from The General Tire and Rubber Company. While these materials were being prepared, attempts were made to lower the average molecular weight of existing prepolymers by the addition of low molecular weight diols.

Binders were prepared using 1,4-dimethylolcyclohexane as part of the prepolymer in Binders 130 and 131 (Table VI) in order to increase the concentration of urethane linkages. The binders contained 1 and 5% of the low molecular diol, respectively, and had calculated crosslink densities of 10^{-5} and 10^{-4} mole branch points/gm. The gel fraction of No. 130, 0.050, was lower than is usual for this type of formulation and may indicate a poor cure. Binder No. 130 has approximately 15% more urethane linkages per gram than Binder No. 76.

1,4-Dimethylolcyclohexane is only partially soluble in these systems and this causes doubts as to the extent of cure. When 5% diol was used, many solid particles were present in the binder indicating a large amount of insolubles. The gel fractions of toluene swollen samples were high, but the effectiveness of toluene as a solvent for this system is not known.

Binders were prepared with hexanediol and pentanediol but octanediol and decanediol were incompatible with the prepolymer. Test results are not yet available.

d. Replacement of CTI

PAPI (polymethylene polyphenylisocyanate) and the cross-linker hexanetriol were studied as possible replacements for CTI. These materials were used because of their availability, but other crosslinkers will also be investigated.

Binders cured with PAPI and HDI are opaque, indicating PAPI was not completely soluble without a plasticizer.

Binders Nos. 136 to 138 and 141 (Table VI) contain varying ratios of PAPI and HDI. The gel fractions of these binders compared with those of Nos. 133-135 indicate the need for more equivalents of PAPI than CTI for binders of equivalent gel fractions. This reflects the lower functionality of or extent of cure with PAPI. PAPI is not completely compatible with Telagen S but it gives cures. Binder No. 142 which was cured with PAPI and contained treated LDP did not cure completely.

Hexanetriol was used in Binders Nos. 143-145. The cross-link densities of Binders Nos. 143 and 144 were calculated to be 10^{-5} and 10^{-4} mole branch points/gm, respectively. Binder No. 145 contains 25% treated IDP and can be directly compared with No. 143. It should be noted that there was very little change in the gel fractions when the plasticizer was added. In

Table VI

COMPOSITION AND PROPERTIES OF TELAGEN S BINDERS^a

| Reference No. | Prepolymer Lot No. | Plasticizer ^b Type | Amount % Wt | HDI/CTI equiv | Cure Time, days at 135°F | Mechanical Properties at 77°F | | | | Mooney-Rivlin | | Estimated Crosslink Density, moles _s chain per cc x 10 ³ | | Gel Fraction \bar{v}_2 |
|------------------|--------------------|----------------------------------|----------------|-------------------|--------------------------|-------------------------------|----------------|-----------|--------------------------|--------------------------|------------|--|------------------|--------------------------|
| | | | | | | σ_s psi | ϵ_s % | E_o psi | C_1 kg/cm ² | C_2 kg/cm ² | from C_1 | From Compression Moduli | from \bar{v}_2 | |
| 77 ^d | 118AH | none | 0 | 4.0 | 7 | 29 | 400 | 400 | 0.10 | 0.22 | 1.0 | - | 1.2 | 0.061 |
| 79 ^d | 118AH | none | 0 | 1.0 | 7 | 82 | 200 | 126 | 0.66 | 0.58 | 6.6 | - | 6.4 | 0.150 |
| 102 | 118AH | none | 0 | 4.0 | 5 | 84 | 280 | 97 | 0.45 | 0.47 | 4.5 | - | 2.8 | 0.093 |
| 103 | 158H | none | 0 | 4.0 | 5 | 78 | 630 | 53 | 0.11 | 0.43 | 1.4 | - | 0.90 | 0.055 |
| 104 | 118AH | none | 0 | 4.0 ^e | 7 | 30 | 286 | 289 | 0.20 | 0.25 | 2.0 | - | 0.48 | 0.040 |
| 105 | 118AH | Toluene | 25 | 4.0 ^f | 7 | 21 | 487 | 20 | 0.06 | 0.13 | 0.6 | 0.73 | 0.80 | 0.052 |
| 111 | 158H | none | 0 | 4.0 ^f | 7 | 27 | 699 | 699 | 0.02 | 0.24 | 0.2 | - | 0.84 | 0.053 |
| 112 | 118AH | none | 0 | 4.0 ^f | 7 | 23 | 370 | 371 | 0.03 | 0.20 | 0.8 | - | 2.4 | 0.091 |
| 113 | 118AH | Toluene | 10 | 4.0 | 6 | - | - | - | - | - | - | - | 1.45 | 0.070 |
| 114 | 118AH | Toluene | 20 | 4.0 | 6 | - | - | - | - | - | - | - | 1.3 | 0.066 |
| 115 | 118AH | Toluene | 30 | 4.0 | 6 | - | - | - | - | - | - | - | 0.82 | 0.054 |
| 122 | 118AE | none | 0 | 4.0 | 6 | - | - | - | - | - | - | - | 1.5 | 0.072 |
| 123 | 118AG | none | 0 | 2.0 | 6 | - | - | - | - | - | - | 1.64 | 2.95 | 0.101 |
| 124 ^a | 118AG | none | 0 | 6.0 | 6 | - | - | - | - | - | - | 1.19 | 0.92 | 0.056 |
| 125 ^a | 118AH | none | 0 | 4.0 | 5 ^h | - | - | - | - | - | - | 1.00 | 0.92 | 0.056 |
| 126 ^a | 118AH | none | 0 | 4.0 | 5 ^h | - | - | - | - | - | - | 1.16 | 1.3 | 0.066 |
| 127 ^a | 118AH | none | 0 | 4.0 | 5 | - | - | - | - | - | - | 0.68 | 0.84 | 0.054 |
| 128 ^a | 118AH ⁱ | none | 0 | 4.0 | 5 | - | - | - | - | - | - | 0.99 | 1.15 | 0.063 |
| 130 | 118AH ⁱ | none | 0 | 5.15 | 8 | - | - | - | - | - | - | - | 0.73 | 0.050 |
| 131 | 118AH | none | 0 | 8.5 | 8 | - | - | - | - | - | - | - | 0.84 | 0.054 |
| 133 | 158H | none | 0 | 2.0 | 7 | - | - | - | - | - | - | 2.24 | 2.45 | 0.092 |
| 134 | 158H | none | 0 | 4.0 | 7 | - | - | - | - | - | - | 0.38 | 0.38 | 0.036 |
| 135 | 158H | none | 0 | 5.0 | 7 | - | - | - | - | - | - | 0.15 | 0.15 | 0.022 |
| 136 ^a | 118H | none | 0 | 0.33 ^j | 6 | - | - | - | - | - | - | 1.17 | 1.9 | 0.080 |
| 137 ^a | 158H | none | 0 | 3.0 ^j | 6 | - | - | - | - | - | - | 0.43 | 1.2 | 0.064 |
| 138 | 158H ^k | none | 0 | 2.0 | 6 | - | - | - | - | - | - | 0.19 | 0.36 | 0.035 |
| 139 | 158H ^k | none | 0 | 2.0 | 7 | - | - | - | - | - | - | 0.75 | 0.95 | 0.057 |
| 140 | 158H | none | 0 | 4.0 ^j | 7 | - | - | - | - | - | - | 0.20 | 0.18 | 0.024 |
| 141 | 158H | none | 0 | 1.0 ^j | 6 | 40 | 530 | 30 | 0.10 | 0.15 | 1.0 | 0.65 | 0.85 | 0.054 |
| 142 | 158H | IDP | 25 | 1.0 ^j | 6 | - | - | - | - | - | - | - | incomplete cure | 0.037 |
| 143 | 118AH | none | 0 | 5.0 ^l | 6 | 26 | 630 | 25 | 0.04 | 0.18 | 0.4 | 0.31 | 0.41 | 0.037 |
| 144 | 118AH | none | 0 | 1.85 ^l | 6 | 52 | 370 | 52 | 0.21 | 0.26 | 2.1 | 1.47 | 1.8 | 0.079 |

Table VI (Cont.)

| Reference No. | Prepolymer Lot No. | Plasticizer ^b Type | Amount % Wt | HDI/CTI equiv | Cure Time, days at 135°F | Mechanical Properties at 77°F | | | | Mooney-Rivlin | | Estimated Crosslink Density, moles _g chain per cc x 10 ³ | | Gel Fraction V ₂ |
|---------------|--------------------|----------------------------------|----------------|-------------------|--------------------------------|----------------------------------|---------------------|---------------------|-----------------------|--------------------------------------|--------------------------------------|--|--|-----------------------------------|
| | | | | | | σ _b psi | ε _b % | ε _s % | E _o psi | C ₁ kg/cm ² | C ₂ kg/cm ² | from C ₁ | Compression Moduli from V ₂ | |
| 145 | 148AH | IDP | 25 | 4.75 ^l | 6 | 12 | 560 | 560 | 4 | 0.04 | 0.01 | 0.4 | 0.32 | 0.033 |
| 155 | 161AHR | none | 0 | 1.0 | 6 | 76 | 180 | 180 | 125 | 0.67 | 0.66 | - | - | 0.14 ^m |
| 156 | 161AHR | none | 0 | 2.0 | 6 | 56 | 285 | 285 | 72 | 0.32 | 0.43 | - | - | 2.45 ^m |
| 157 | 161AHR | none | 0 | 4.0 | 6 | 29 | 690 | 690 | 29 | 0.04 | 0.23 | - | - | 0.091 |
| 158 | 161AHR | none | 0 | 6.0 | 6 | 8.3 | 720 | 720 | 21 | 0.01 | 0.13 | - | - | 0.041 |
| 159 | 161AHR | IDP | 25 | 2.0 | 6 | 24 | 280 | 280 | 23 | 0.18 | 0.07 | - | - | 0.020 |
| 160 | 161AHR | IDP | 25 | 4.0 | 6 | - | - | - | - | - | - | - | - | 0.068 |
| 168 | 148AH ^o | none | none | 4.0 | 7 | 71 | 356 | 360 | 115 | 0.25 | 0.27 | 2.5 | - | 0.028 |
| 171 | 148AH | none | none | 4.0 ^p | 5 | 54 | 440 | 440 | 42 | 0.21 | 0.10 | 2.1 | - | 0.078 |
| 172 | 148AH | none | none | 2.0 ^p | 5 | 83 | 350 | 350 | 354 | 0.43 | 0.07 | 4.3 | - | - |
| 173 | 148AH | Ansul | 25 | 4.0 | 10 | 30 | 294 | 297 | 37 | 0.26 | 0.03 | 2.6 | - | 0.071 |
| 176 | 168H | Ether 181 | none | 4.0 | 7 | - | - | - | - | - | - | - | - | 0.054 |
| 177 | 175B | none | none | 2.0 | 7 | - | - | - | - | - | - | - | - | 0.092 |
| 178 | 168H | none | none | 2.0 | 6 | 100 | 240 | 240 | 151 | 0.74 | 0.35 | 7.4 | - | 0.105 |
| 179 | 168H | none | none | 4.0 | 6 | 85 | 466 | 466 | 95 | 0.28 | 0.29 | 2.8 | - | 0.078 |
| 180 | 168H | none | none | 6.0 | 6 | 70 | 443 | 445 | 100 | 0.22 | 0.29 | 2.2 | - | 0.059 |

^aNGO/OH = 1.0 (except No. 137, 2.0), .04% FeAA cure catalyst (except Nos. 125 and 126, 0.05% Nix D-22; and Nos. 127 and 128, 0.2% Nix D-22).

^bIDP passed through column of SiO₂, toluene redistilled from sodium and Ansul Ether 181 redistilled from Na.

^cWhen other curing systems used, this column gives the equivalents ratio of extender to crosslinker.

^dPrepared and tested in Phase One.

^eHDI replaced with Nacconate H-12.

^fHDI replaced with TDI.

^gUnsaturated analog of 148AH.

^hCured at room temperature.

ⁱBinder 130 contains 1% and Binder 131, 5% of 1,4-dimethylolcyclohexane.

^jCTI replaced by PAPI.

^kBinders prepared assuming equivalent weight of 1190

^lHexanetriol used as crosslinker.

^mEstimated from E_o.

ⁿCrosshead limit.

^oContains pentanediol.

^pPrenolymers to CTRO ratio.

the usual binder preparations, the gel fraction would decrease more than that shown in This case.

The gel fractions of Binders Nos. 77 and 79 which have theoretical crosslink densities of about 10^{-5} and 10^{-4} mole branch points/gm when cured with CTI, are higher than those of binders containing hexanetriol. Also the gel fraction of Binder No. 77 should be closer to 0.090 than to the observed 0.060. This corroborates earlier work under Contract AF 04(611)-10386 which indicated hexanetriol was not as good a crosslinker as CTI.

A binder, containing glycerol triricinoleate, GTRO, was prepared for comparison. GTRO was compatible with this binder system and appeared to give a complete cure. Data will be reported when available.

e. Room Temperature Cures

Niax D-22 (dibutyltin dilaurate) was used as a catalyst for room temperature cures. A binder masterbatch was prepared and divided into two portions. To one portion was added 0.05% catalyst and to the other 0.2% catalyst, then each portion subdivided again and cured for 5 days at 135°F or at room temperature in a desiccator. Both cure temperatures gave equal gel fractions (equivalent cures).

The results are shown in Table VI, Binders 125 to 128. These results show that the room temperature cures were as good as those at 135°F. One attempt was made to prepare a propellant using Niax D-22 as the cure catalyst. While the castability of the propellant was poor, this system will be investigated further.

Catalyst studies made to further the effort on this objective are reported under the Task Three section of this report.

f. Unsaturated Binders

Binders Nos. 122-124 were prepared to compare an unsaturated prepolymer with a saturated one. These unsaturated binders were prepared at HDI to CTI ratios of 2, 4 and 6 (Table VI). A plot of gel fraction vs crosslinker content (Figure 3), indicates that the unsaturated prepolymer will cure with HDI only. If the gel fractions are correct, the results may be explained by additional crosslinks in this prepolymer due to oxidative crosslinking of chains.

g. Replacements for HDI

Binders were made using various isocyanates as replacements for HDI. For example, Binders 111-112 (Table VI) contained TDI as a replacement for HDI and can be compared with Binders 102 and 103. These binders also serve to compare Prepolymers 148AH and 158H. The gel fractions

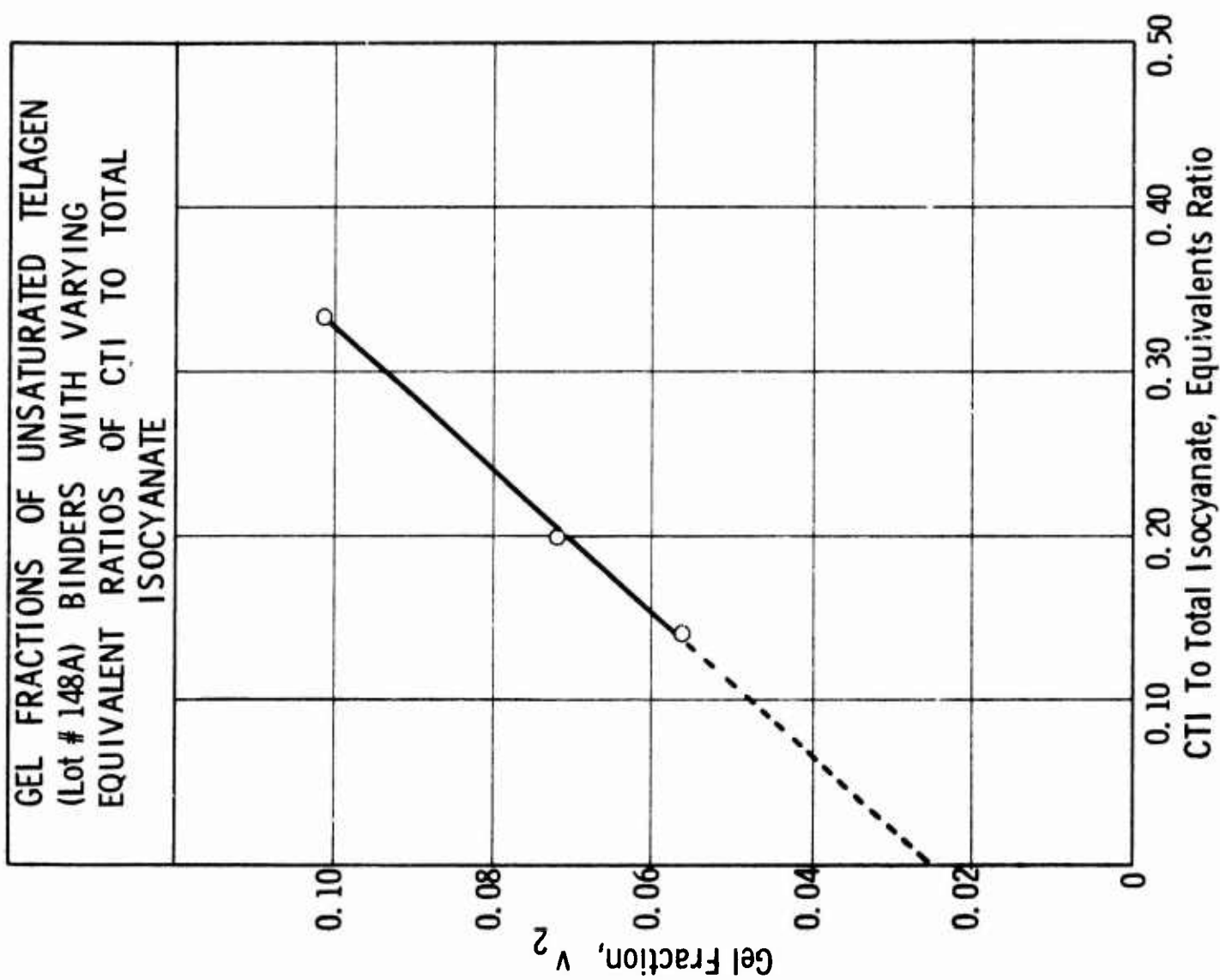


Figure 3



of Binders 111 and 112 are suspect because they are too high compared to the E_0 and C_1 values. The mechanical properties data and the Mooney-Rivlin C_1 indicate that the HDI binders are better. The results also show that Pre-polymer 148AH has a higher functionality than Prepolymer 158H.

Binder 104, cured with Nacconate H-12, had lower gel fraction and poorer mechanical properties than did the HDI cured Binder 102.

h. Plasticizer Studies

Only a minimum effort has been expended on plasticizer studies. Ansul Ether 181, which seriously interfered with the cure of Telagen S binders and propellants, was purified by refluxing over sodium for several days, filtering, then vacuum distilling it from more sodium. The plasticizer was used in a small binder sample which cured satisfactorily. Previously, a binder containing unpurified plasticizer did not cure. The binder is hazy, indicating that the plasticizer is not completely compatible.

Binders 105 and 113 to 115 were prepared with toluene as the plasticizer. The toluene will be removed under vacuum and the binders will be allowed to imbibe a plasticizer to determine plasticizing effects on a binder prepared in the presence of a diluent, but without cure effects. Possibly the effect of plasticizer at low temperatures may be determined in this way.

The gel fractions of these toluene binders are rather low considering that toluene does not interfere seriously with isocyanate curing agents.

It was postulated that if more catalyst were added to plasticized binders and propellants, the faster rate of cure would overcome plasticizer interactions and other effects which inhibit the cure. Squalene, known to interfere with cure, was used as the plasticizer in four binders. The catalyst, FeAA, was varied from 0.075% to 0.3% and the samples kept at 135°F for 6 days. After curing, the binders were tested by swelling and all had gel fractions between 0.054 and .056. The level of catalyst within these limits had no effect. Apparently the catalyst catalyzed the cure-interference reactions as well as the cure reactions.

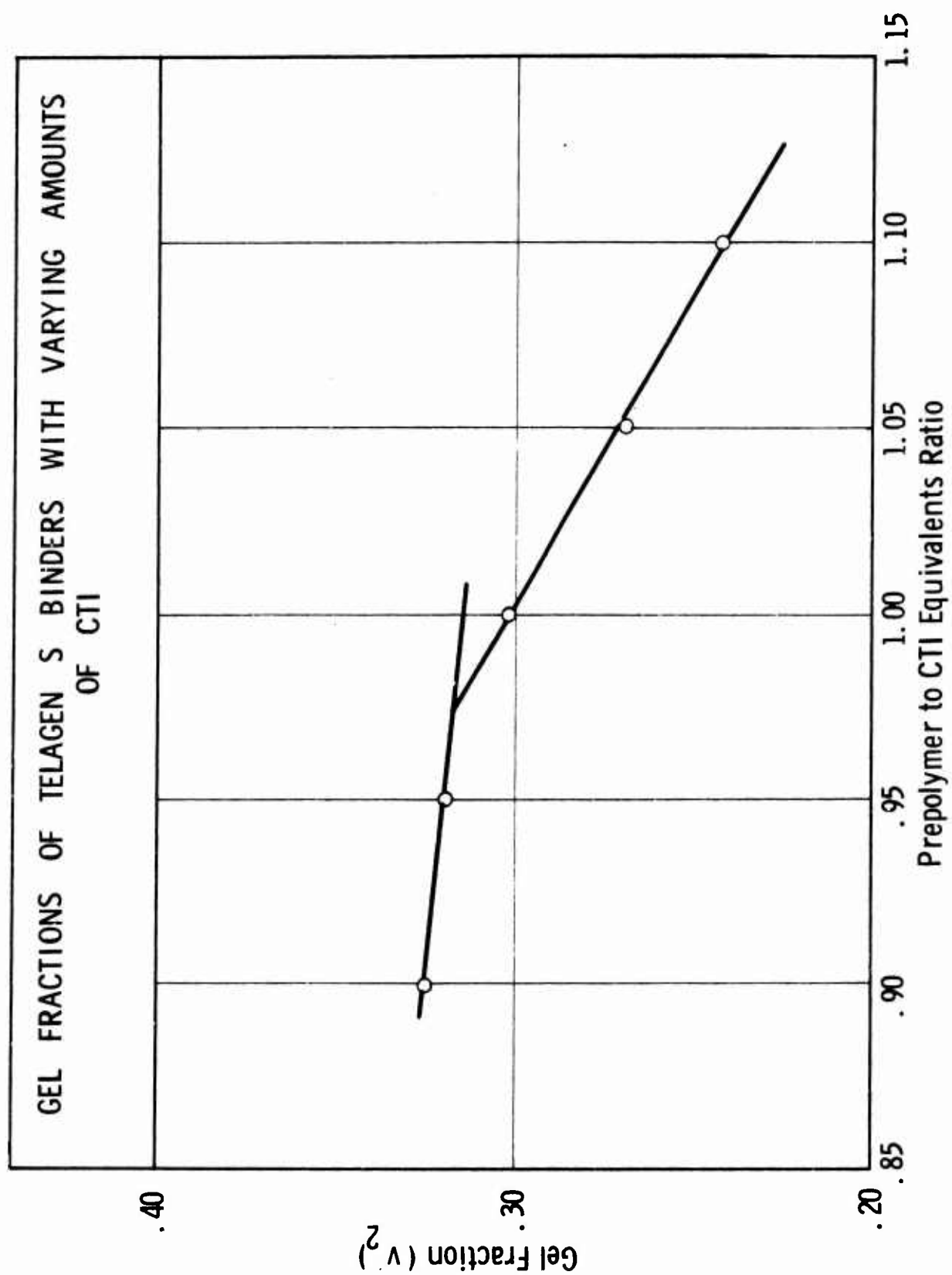
i. Cure Stoichiometry

Telagen S (Lot 242AM-148AH) was reacted with various amounts of CTI. The binders were swollen and the results are shown in Figure 4. With excess isocyanate, the gel fraction increased slowly. The excess isocyanate was either reacting with the urethane linkages or homopolymerizing slowly.

j. Prepolymer 161AHR

Binders were made of the new prepolymer, Lot 242AM-161AHR.

UNCLASSIFIED



-16-

UNCLASSIFIED

Figure 4

These binders (Nos. 155-160) are listed in Table VI. Although testing is not complete, the mechanical properties are similar to those of binders prepared from Prepolymer 148AH.

k. Propellant Studies

Propellants were made on both the 400-gram and 3200-gram scale. The composition and properties are reported in Table VII. Propellants 67-98-2 and -24 are samples from different cartons of 125-lb batch of propellant which is now being aged.

Propellant No. 9569, was prepared to replace aging samples lost when water leaked into the 77°F, 50% humidity oven. Four bars of this propellant were cut and will be used to spot check the aging results obtained at the above conditions. Propellant No. 9614 was prepared using dioctyl sebacate as the plasticizer in order to compare this plasticizer with IDP in propellants aged at 170°C and 25% humidity.

Two propellants were made using Prepolymer 158H, Nos. 9570 and 9615, to compare effects of an NCO to OH ratio of 1.00 and 1.02. The higher NCO ratio gave a better product, but required a longer cure period. The longer cure time was also observed in Propellants 137 and 138. After 7 days of cure, the propellant with the higher NCO content was not as hard as the other, but after about 14 days, Propellant 138 was harder. The explanation may be that at the NCO to OH ratio of 1.02, the binder ingredients are not stoichiometric and therefore would not attain as complete a cure (or achieve an equivalent hardness) as the binder in the propellant with the stoichiometric NCO to OH ratio. Thus an initially lower hardness is observed. However, with time slower secondary reactions of the excess isocyanate groups take place to increase the crosslink density (and hardness) beyond that obtained with the stoichiometrically formulated propellants. Figure 4 indicates that secondary crosslinking reactions do occur in the presence of excess isocyanate. The secondary reactions may be either dimerization of the isocyanate or allophanate formation.

Prepolymer 161AHR needs a lower HDI to CTI ratio, that is, more crosslinker, to achieve a given modulus. This reflects its lower functionality which was established by the binder studies.

A 125-lb batch of propellant with the prepolymer 161AHR will be mixed in the near future.

Hexanetriol was used as the crosslinker in Propellant 1601. The propellant is soft and emphasizes the problems that have been encountered with this triol. Possibly it is too polar for this system. It is unlikely the hexanetriol will be a suitable replacement for CTI.

PAPI was used as the curing agent in Propellant 1602 and it gave a good, fast cure. The values of the Shore A hardness and mechanical

Table VII

COMPOSITION AND PROPERTIES OF TELAGEN S PROPELLANTS^a
(125-lb Batches)

| Reference No. | Prepolymer Lot No. | HDI/CTI | NCO/OH | Cure Time, days at 135°F | Shore A Hardness | | Mechanical Behavior at 77°F | | | |
|---------------------|--------------------|---------|--------|--------------------------|------------------|----------|-----------------------------|----------------|----------------|-----------|
| | | | | | Top | Side | σ_b psi | σ_t psi | ϵ_b % | E_o psi |
| 67-98-2 | 158H | 3.5 | 1.02 | 16 | 68 | 57 | 123 | 116 | 35 | 605 |
| 67-98-24 | 158H | 3.5 | 1.02 | 16 | 68 | 58 | 123 | 116 | 35 | 610 |
| (3200-gram Batches) | | | | | | | | | | |
| 9569 | 148AH | 4.0 | 1.02 | 7 21 | 62 68 | 56 | 119 | 118 | 32 | 546 |
| 9570 | 158H | 3.5 | 1.02 | 7 21 34 | 67 68 | 53 | 81 | 77 | 44 | 291 |
| 9614 ^a | 148AH | 4.0 | 1.02 | 7 8 20 | 55 63 66 | 54 59 | 114 | 113 | 33 | 514 |
| 9615 | 158H | 3.5 | 1.0 | 7 8 20 34 | 44 47 50 | 39 39 | 64 | 59 | 51 | 231 |
| 137 | 158H | 3.0 | 1.0 | 7 14 28 | 45 43 53 | 42 | 84 | 78 | 45 | 271 |
| 138 | 158H | 3.0 | 1.02 | 7 14 28 | 53 62 72 | 37 | 60 | 55 | 51 | 190 |
| | | | | | | 62 | 141 | 139 | 38 | 581 |

Table VII (Cont)

| Reference No. | Prepolymer Lot No. | HDI/CTI | NCO/OH | Cure Time, days at 135°F | Shore A Hardness | | Mechanical Behavior at 77°F | | | |
|--------------------|--------------------|------------------|--------|--------------------------|--------------------|----------------|-----------------------------|----------------|----------------|----------------|
| | | | | | Top | Side | σ_u psi | σ_b psi | ϵ_u % | ϵ_b % |
| 1300 ^a | 161AHR | 3.5 | 1.02 | 8 12 21 | 40 43 47 | 26 42 45 | 66 | 62 | 43 | 48 |
| (400-gram Batches) | | | | | | | | | | |
| 1601 | 148AH | 2 ^b | 1.03 | 4 7 15 | soft soft 21 | - - - | - | - | - | - |
| 1602 | 148AH | 1 ^c | 1.02 | 4 7 15 | 75 68 75 | 60 75 70 | - | - | - | - |
| 1603 | 161AHR | 3.5 | 1.02 | 4 7 15 | 18 35 44 | - 10 48 | - | - | - | - |
| 1604 | 161AHR | 3.0 | 1.02 | 4 7 15 | 31 54 59 | - 31 61 | - | - | - | - |
| 1761 | 161AHR | 3.5 | 1.0 | 7 10 | 45 48 | 34 40 | - | - | - | - |
| 1762 | 161AHR | 3.0 | 1.0 | 7 10 | 48 50 | 44 46 | - | - | - | - |
| 1912 | 148AH | 4.0 ^d | 1.02 | 4 | - | - | - | - | - | - |
| 1913 | 161AHR | 3.0 | 1.02 | 4 | 32 | - | - | - | - | - |
| 1914 ^e | 148AH | 4.0 | 1.02 | 4 7 | 67 65 | 47 67 | - | - | - | - |
| 1915 ^f | 158H | 3.5 | 1.0 | 4 | - | - | - | - | - | - |

*Please see following page for footnotes.

Table VII (Cont)

Footnotes

^aAll propellants contain 88 wt% solids, 25% IDP purified by passing through silica gel (except 9614 which contains DOS), and 0.002% FeAA and 0.006% HAA.

^bPrepolymer/hexanetriol.

^cHDI/PAPI.

^dTDI replaced HDI.

^eContains no HAA.

^fContains burning rate additive AR, supplied by Dr. R. S. Bruenner (AGC).

properties indicate that a higher HDI to PAPI ratio should be used to achieve more optimum product characteristics. PAPI may be a suitable replacement for CTI and is being investigated further.

Propellant 1914 was mixed at 110°F, with only FeAA as the catalyst and no HAA to modify the catalyst activity in order to obtain a cure at lower temperature. The castability of this propellant was poor and it cured to a much higher modulus. The higher prepolymer viscosity at lower temperatures may limit the processing of these propellants.

1. Burning Modifiers

Effort to define some combustion properties of Telagen S propellants are being made. Propellant 1915, Table VII, contains a burning rate modifier, but burning data are not available.

Pertinent to this effort is work done by Dr. W. S. Schmidt at Aerojet under Contract NAS-1-6323. He studied the uncatalyzed burning rates of two propellants; one with hydroxy-terminated, butadiene polymer, 148A and with the corresponding hydrogenated prepolymer 148AH. The 88 wt% solids propellants had the same burning rates (Figure 5). The pressure exponent is about 0.36 in the range 100 to 600 psia and about 0.9 at 1000 to 3000 psia. Between 600 and 1000 the exponent is increasing.

2. Task Two

a. Introduction

Task Two involves the determination of the compatibility of the prepolymers and curing agents with combinations of advanced oxidizer and advanced fuel. Model compounds are being used to study the binder component interactions with the fuels and oxidizers and attempts are being made to improve systems which have poor compatibility. Compatible systems will be evaluated ballistically at the 1-lb scale.

b. Curing Agents for Advanced Oxidizers

1) Acid Anhydrides

Studies of acid anhydrides as curing agents for hydroxy-terminated Telagen S prepolymer with the oxidizer HAP were initiated. Acetic anhydride, a model acid anhydride, was reacted with a 2-octanol in the presence of HAP. The chromatographic analysis of the model binder system (Figure 6) indicated that the reaction is complete after 15 minutes and that > 99% of the theoretical ester product (2-octyl acetate) is formed. The rates of reaction of 2-octanol with dodecenylsuccinic and phthalic anhydrides were investigated. The results are shown in Table VIII.

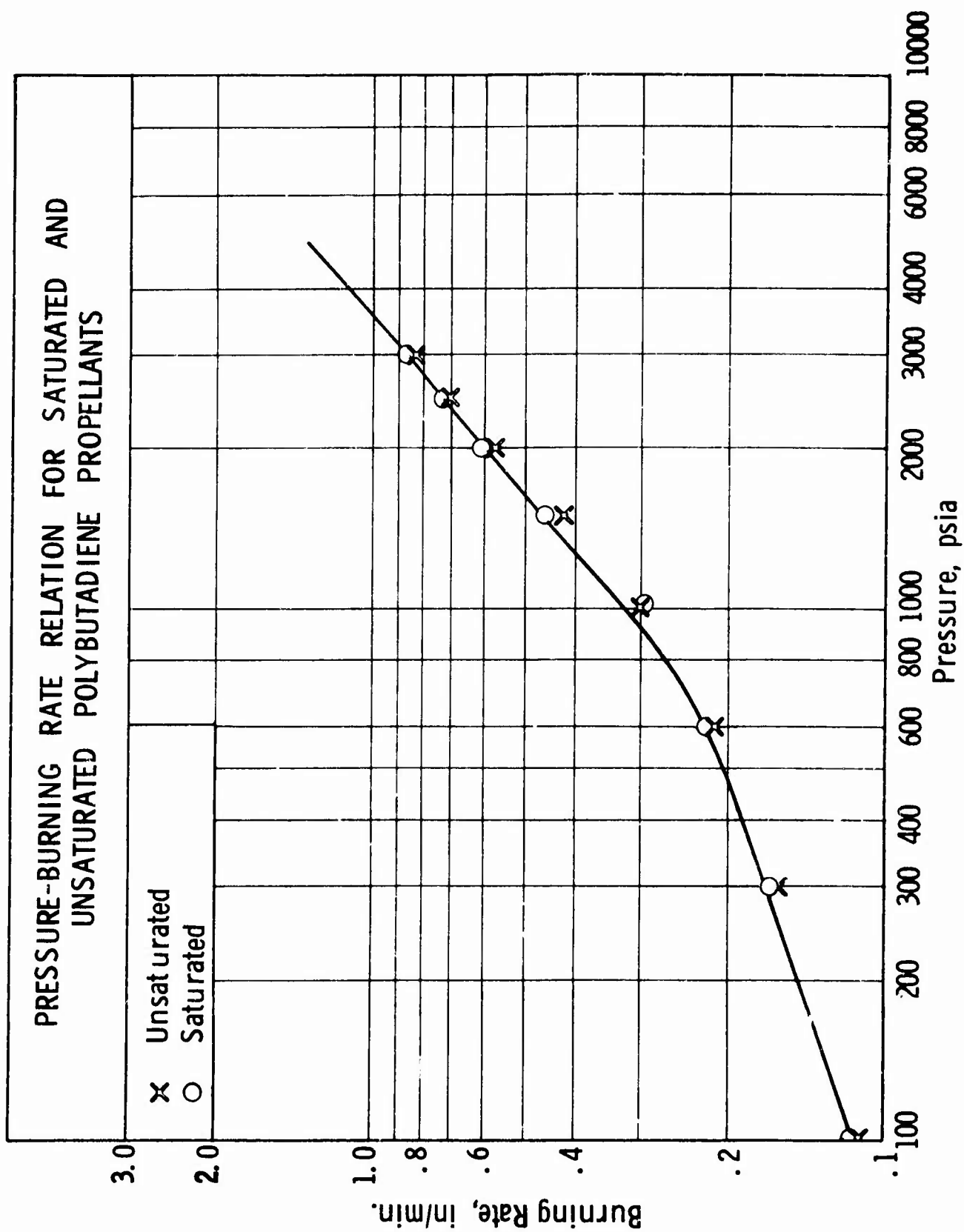
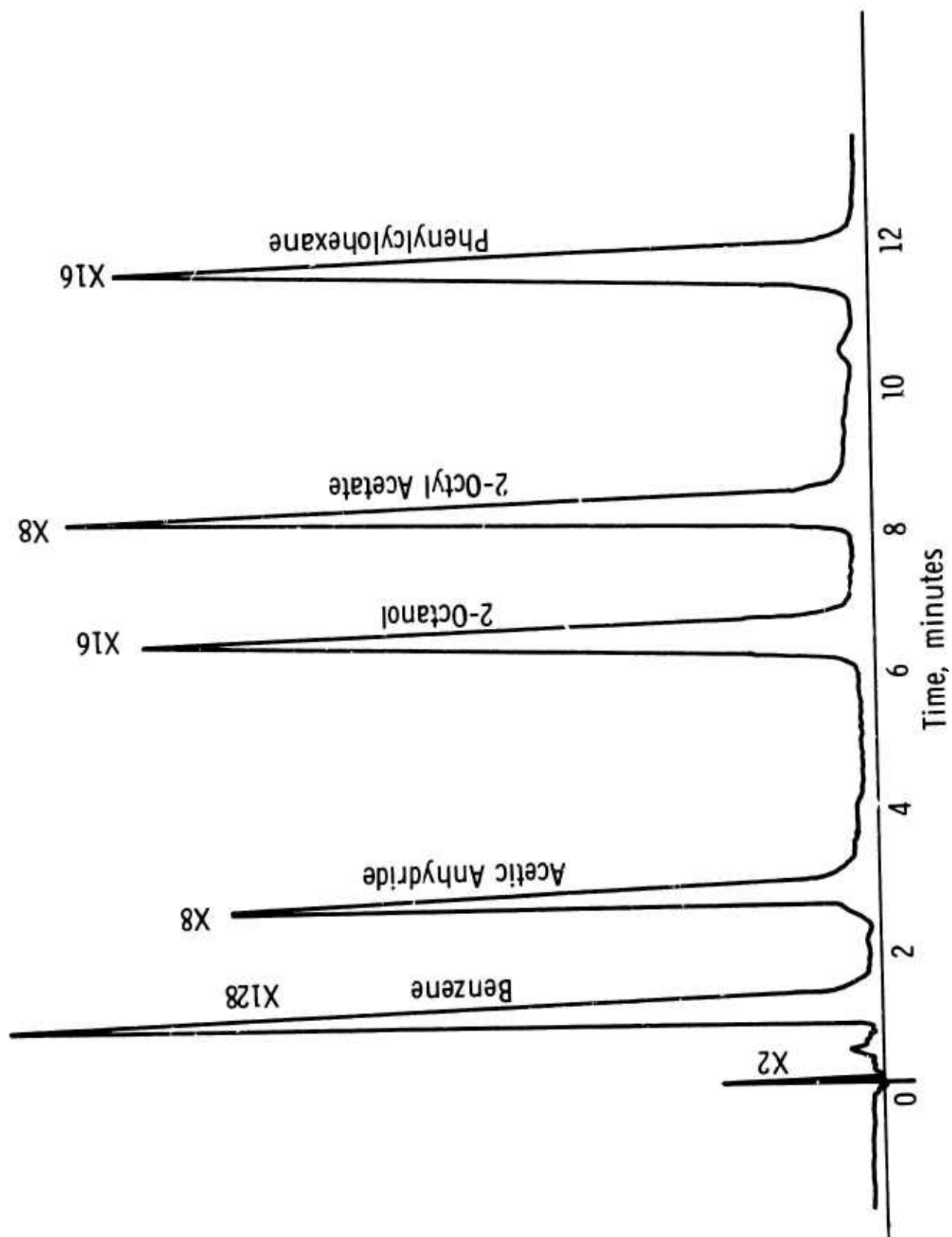


Figure 5

CHROMATOGRAM OF ACETIC ANHYDRIDE - 2-OCTANOL IN BENZENE

UNCLASSIFIED



UNCLASSIFIED

Figure 6

Table VIII

REACTION OF ACID ANHYDRIDES WITH 2-OCTANOL IN THE
PRESENCE OF HAP AT ROOM TEMPERATURE

| <u>Anhydride</u> | <u>Time, min</u> | <u>Compound remaining, %</u> | | |
|-------------------|------------------|------------------------------|------------------|----------------|
| | | <u>Alcohol</u> | <u>Anhydride</u> | <u>Product</u> |
| Acetic | 15 | 0 | 0 | 99 |
| Dodecenylsuccinic | 45 | 58.8 | 57.9 | - |
| Phthalic | 780 | 90.0 | 90.0 | - |

The reactions of the acid anhydrides with 2-octanol are quantitative in yield and the rates of reaction are very rapid and strongly dependent on the type of anhydride. The aromatic anhydrides were slowest and their potential as curing agents is being investigated further.

2) Cyclic Imides

The compatibility and fast reaction of acid anhydrides in the presence of HAP suggested a study of the less reactive cyclic imides as potential curing agents. A number of cyclic imides were reacted with 1-octanol in the presence of HAP. A typical chromatogram is shown in Figure 7. The N-n-butylsuccinimide and N-n-butylphthalimide showed no reaction with the alcohol after 18 hours at 50°C. The unsubstituted phthalimide did not react under the same conditions but the unsubstituted dodecenylsuccinimide showed 10% stoichiometric reaction.

Studies of the use of cyclic imides as possible crosslinking agents were continued. Various cyclic imides were prepared and reacted with 1-octanol in the presence of HAP (see Table IX). The present data indicate that cyclic imides are stable in the presence of HAP, and that HAP has no catalytic affect on the reaction of imides with alcohols. Unless, however, an effective catalyst can be found, the cyclic imides are unsuitable as crosslinking agents for low temperature cure propellants. Work along these lines has been discontinued.

3) Azetidines

Acyl and aroyl azetidines have been found to be considerably less susceptible to acid catalyzed polymerization than the related aziridines. Synthesis of a model compound to test its compatibility with the various advanced fuels and oxidizers and reactivity as a crosslinking agent has been initiated.

GAS-LIQUID CHROMATOGRAM OF 1-OCTANOL, HEXAHYDROPTHALIMIDE,
AND PHENYLCYCLOHEXANE IN BENZENE

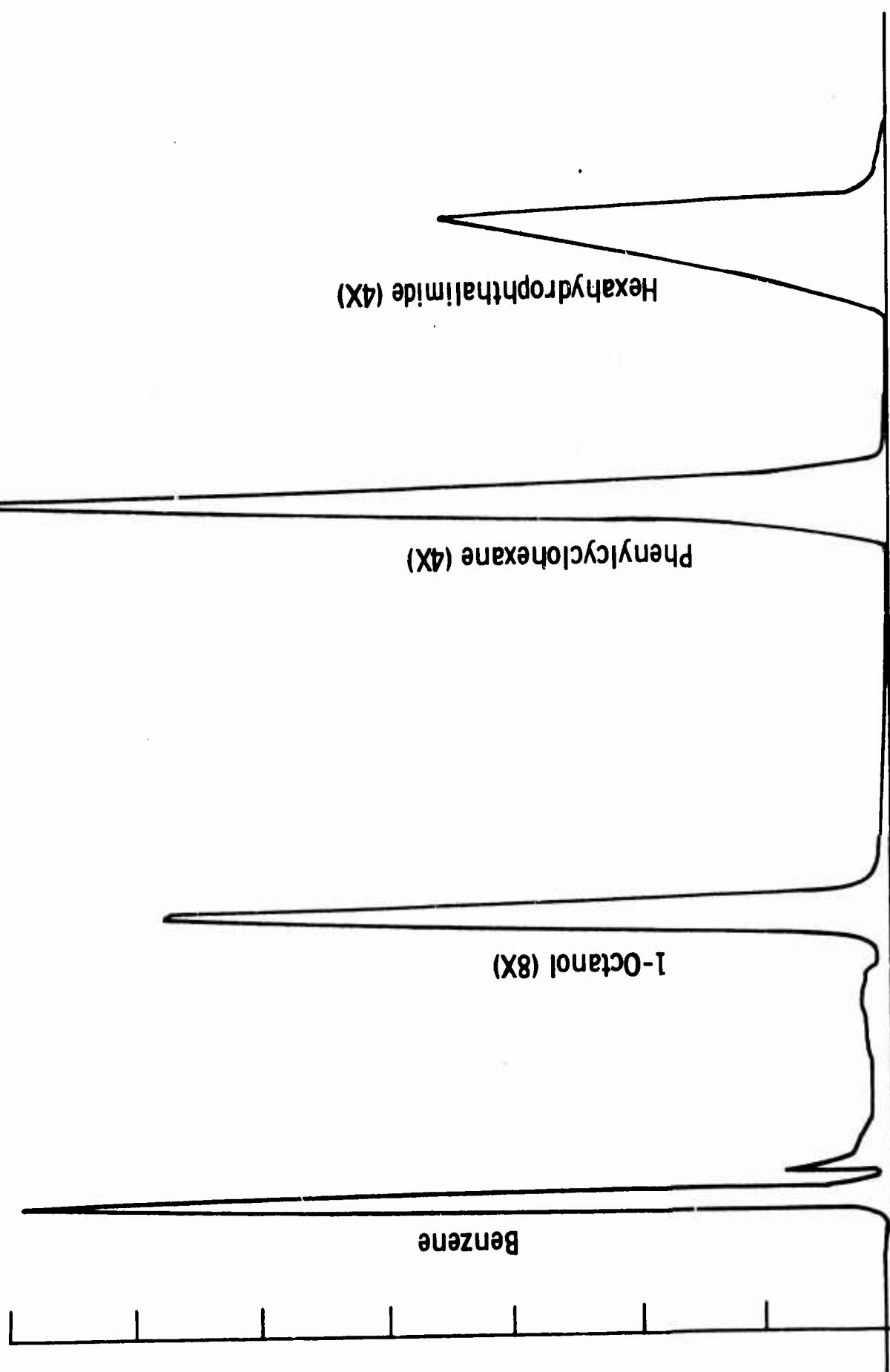


Table IX

REACTION OF VARIOUS CYCLIC IMIDES WITH 1-OCTANOL
IN THE PRESENCE OF HAP AT 50°C

| <u>Cyclic Imide</u> | <u>Time Days</u> | <u>Observation</u> |
|--|----------------------|--------------------|
| N-Butyltetrabromophthalic | 3 | no reaction |
| N-Butylmaleic | 3 | no reaction |
| Nadic methyl | 3 | no reaction |
| Hexahydrophthalic | 1 | ~ 5% |
| 3,4,5,6,7,7-Hexachlorobicyclo[2.2.1] hepta-4,5-ene-1,2-dicarboxylic | 1 | no reaction |

3. Task Three

a. Introduction

The testing of curing agents and catalysts for achieving a room temperature cure and obtaining a suitable replacement for CTI are the main studies for Task Three. The synthesis of curing agents on an "as needed" basis is also being done.

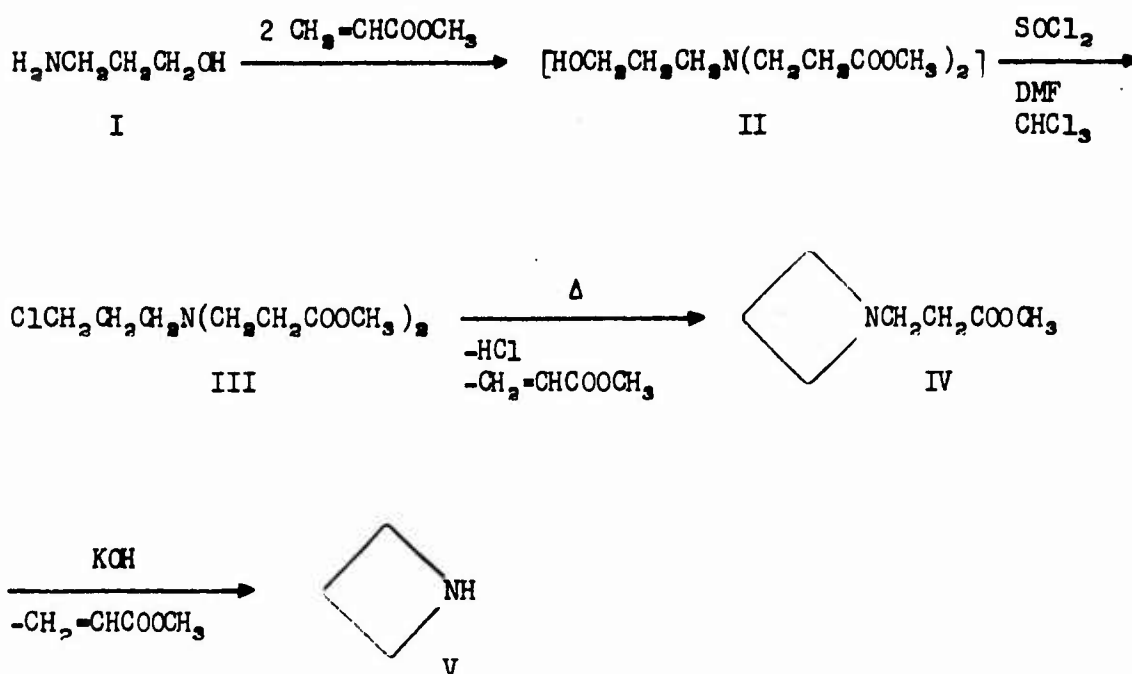
b. Synthesis of Imides

Phthalimide and dodecenylsuccinimide were prepared by reacting the anhydride with an excess of concentrated ammonia and refluxing the mixture for 2 hours. The water and ammonia were removed by distillation to yield the desired product.

The corresponding N-n-butyl derivatives were prepared in a similar manner by reacting the appropriate anhydride with a mole of n-butylamine. Results of tests with these materials are described in Section IV.B.2.b. (2).

c. Synthesis of Azetidine

1-(2-carbomethoxyethyl)azetidine (IV) has been prepared from the cyclization of dimethyl N-(3-chloropropyl)-2,2'-iminopropionate (III) by the method of Wadsworth⁽⁵⁾.



The infrared spectra of the crude compounds II, III, and IV are shown in Figures 8-10. Compound (IV) will be converted to the parent azetidine (V) which will then be used to prepare various N-aryl or acyl azetidines for compatibility studies with advanced fuels and oxidizers.

d. Room Temperature Cures

A screening of several catalysts was carried out to find suitable candidates for a room temperature cure. A 0.2N solution of Prepolymer 148AH and n-butyl isocyanate was prepared in toluene. Aliquots (33-ml) were transferred to volumetric flasks which contained 0.1 gm of catalyst. Five-ml aliquots were periodically analyzed for isocyanate, Table X.

The sampling techniques were not entirely suitable for the active catalysts because the initial points show considerable reaction. However, it is apparent that FeAA, Niox D-22 and Thermalite-25 are the most active. FeAA and Niox D-22 were used in propellants mixed at 110°F, but the castability of these was marginal.

4. Task Four

a. Introduction

Task Four includes Phase Four (propellants in aging before March 1967) and also involves the aging of propellants prepared under Tasks One and Two. It further includes the testing at 350°F of selected Task One propellants and the temperature cycling of propellants made with CTI replacement.

INFRARED SPECTRUM OF $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{COOCH}_3)_2$

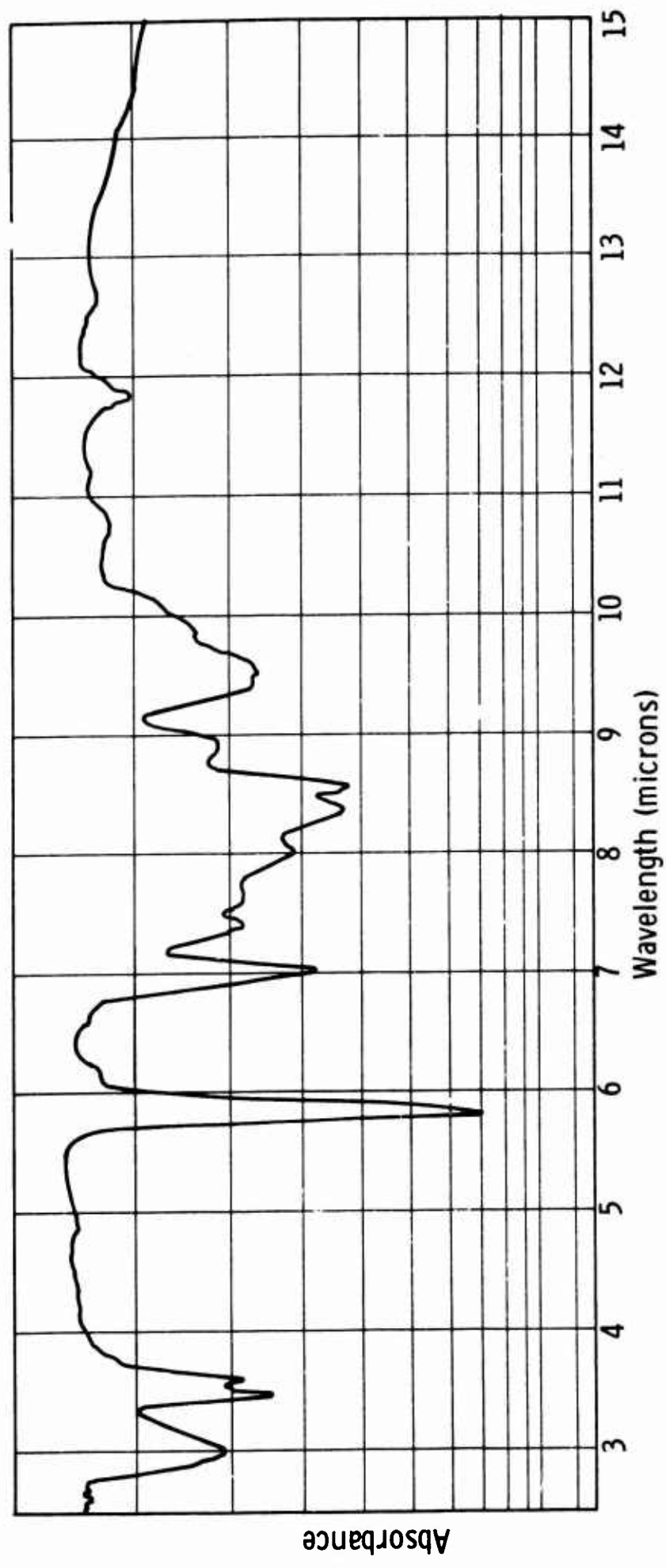
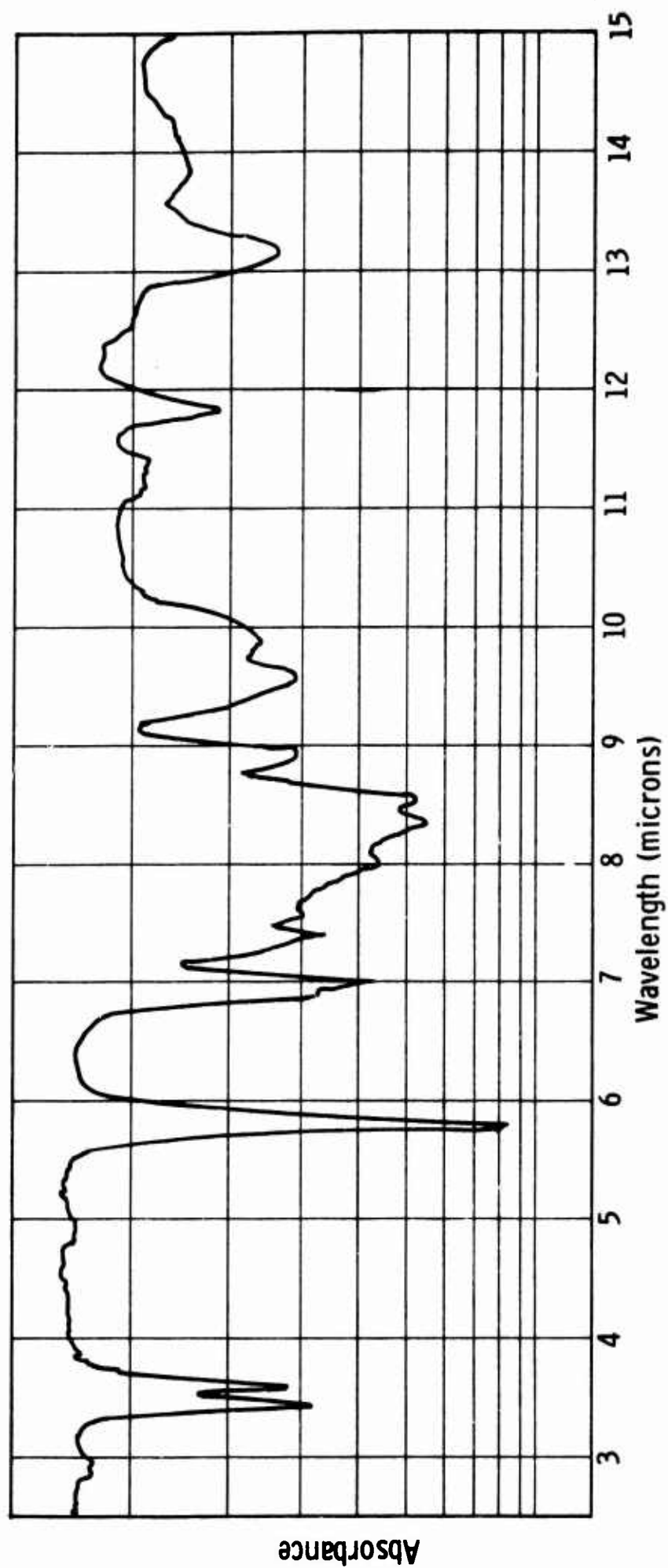


Figure 8

INFRARED SPECTRUM OF $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{COOCH}_3)_2$



INFRARED SPECTRUM OF C1CCN(C1)CCOC(=O)C

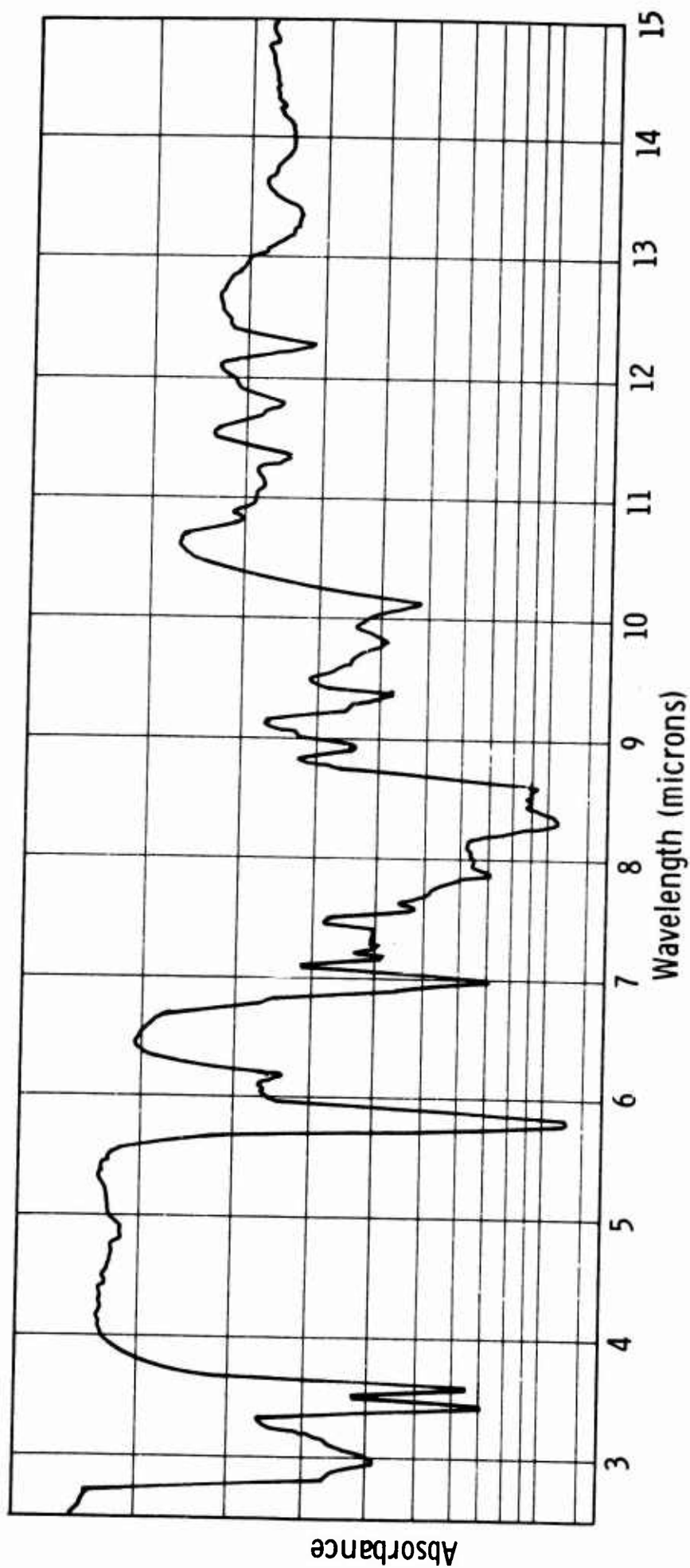


Figure 10

Table X

CATALYSIS OF THE REACTION OF N-BUTYL ISOCYANATE (0.2N) WITH
PREPOLYMER 148AH (0.2N) IN TOLUENE AT ROOM TEMPERATURE^a

| Time hrs | Catalyst ^b | | | | | | | |
|----------------|-----------------------|-------------|--------------|---------------------|---------------------|-------|------------------|--------------|
| | FeAA | FeAA HAA | Niax D-22 | Niax D-22 HAA | Stannous Octoate | COAA | Thermalite 25 | T-18 None |
| 0 ^c | 0.691 | 0.988 | 0.789 | 0.703 | 0.872 | 0.908 | 0.772 | 0.988 0.99 |
| 4.5 | - | - | - | 0.243 | 0.778 | 0.836 | 0.216 | 0.920 - |
| 18 | 0.017 | 0.570 | 0.023 | - | - | - | - | - - |
| 24 | | - | | 0.029 | 0.537 | 0.625 | 0.009 | 0.665 - |
| 90 | | 0.190 | | | | 0.195 | | 0.588 |
| 120 | | - | | | | | | |
| 162 | | 0.103 | | | | | | |

^a Meq. isocyanate/5-ml aliquot is shown in table.

^b Catalyst = 0.01 gm/33-ml, HAA = 0.03 gm/33-ml; FeAA = Ferric acetylacetonate, HAA = acetylacetone, Niax D-22 = dibutyltin dilaurate, CoAA = cobalt acetylacetonate, T-25 and T-18 = tin salts.

^c Not a true zero time since it includes time to mix and to take first sample.

b. Conventional Propellants

The propellants for the aging program were cut into blocks, half of which were wrapped in aluminum foil. Wrapped and unwrapped samples were aged at the conditions shown in Table XI. A Minuteman Wing VI second stage propellant was included as a control. The Telagen S propellants being aged include Batch Nos. 66-954 and 67-98.

The control propellant, Minuteman Wing VI (No. 21-3066, DWM 001) was used in the qualification of prepolymers for production motors. After the regular 12-day cure cycle, this propellant had the following properties, $\sigma_u/\sigma_b/e_u/e_b/E$, 90/-/34/45/425. After this propellant had been held at room temperature for 6 weeks, pressed bars had the following properties, 108/-/22/32/760. These changes are not uncommon, because of the post cure immediately following the cure cycle. Later, when blocks were cut from liner

boxes for the aging program, the properties were 135/133/16/19/1250. Again, the changes were partially due to post cure, and also to the fact that the bars were milled and that the orientation of the samples was varied. Thus, before the present aging program started, a considerable post cure had occurred in the control propellant at room temperature. This rapid a post cure is unusual, but the latter values for the properties have been used as control values. The aging data is summarized in Tables XII - XX.

Table XI
AGING CONDITIONS

| <u>Condition No.</u> | <u>Temp °F</u> | <u>Atmosphere</u> | <u>Relative Humidity, %</u> |
|--------------------------|--------------------|-----------------------------|---------------------------------|
| 1 | -75 | carbon dioxide, stagnant | 100 |
| 2 | 0 | carbon dioxide, stagnant | 100 |
| 3 | 77 | nitrogen, stagnant | 5 |
| 4 | 77 | nitrogen, stagnant | 50 |
| 5 | 77 | air, circulating | 25 |
| 6 | 77 | air, circulating | 50 |
| 7 | 77 | air, stagnant | 80 |
| 8 | 170 | air, circulating | 25 |
| 9 | 170 | air, circulating | 80 |

After 2 months of aging, only a few generalizations can be made since aging trends have developed only at 170°F. No discernible changes have occurred at either -75 or 0°F for any of the propellant and at 77°F for the Telagen S propellants. There are some incipient signs (very difficult to establish for certainty) of degradation of the Minuteman propellant at 77°F. Thus, note the lower moduli for 9 week data in Tables XV, XVI, XVII, and XVIII where the relative humidity was 25% or higher, but no modulus change in Table XIV where the relative humidity was 5%. These observed changes are difficult to separate from the experimental error, but data for 26 weeks, which should be available soon, may establish the trend more forcefully.

Table XII
MECHANICAL BEHAVIOR OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT -75°F AND 100% RELATIVE HUMIDITY IN CARBON DIOXIDE ENVIRONMENT

| Time in Aging weeks | Mechanical Properties at 77°F, $\sigma_u/\sigma_b/\epsilon_u/\epsilon_b/E$ | | | | | |
|---------------------------|--|-------------------|---------------------------------|------------------|-------------------|---------------------------------|
| | Unwrapped | | | Al Foil Wrapped | | |
| | Telagen S | | Minuteman | Telagen S | | Minuteman |
| | 66-954 | 67-98 | | 66-954 | 67-98 | |
| 0 | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b |
| 1 | - | 129/123/39/42/770 | - | - | 131/124/31/42/770 | - |
| 2 | 111/96/21/30/826 | 141/136/35/43/743 | 135/133/16/19/1330 | 114/96/22/32/843 | 132/126/31/40/852 | 124/123/18/20/1009 |
| 4 | 115/100/24/33/754 | 132/123/33/44/756 | 136/130/16/22/1306 | 115/94/21/32/856 | 130/123/33/44/712 | 134/130/17/22/1173 |
| 9 | 111/100/23/30/843 | - | 128/124/17/21/1160 | 105/92/21/30/802 | - | 121/118/19/24/950 |

^a Propellants all contain 88 wt% solids.

^b These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XIII

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 0°F AND 100% RELATIVE HUMIDITY IN CARBON DIOXIDE ENVIRONMENT

| Time in Aging weeks | Mechanical Properties at 77°F, $\sigma_u/\sigma_b/\epsilon_u/\epsilon_b/E$ | | | | | |
|---------------------------|--|-------------------|---------------------------------|-------------------|-------------------|---------------------------------|
| | Unwrapped | | | Al Foil Wrapped | | |
| | Telagen S | | Minuteman | Telagen S | | Minuteman |
| | 66-954 | 67-98 | | 66-954 | 67-98 | |
| 0 | 100/93/24/28/650 | 123/-/34/45/605 | 135/133/16/19/1250 ^b | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b |
| 1 | 112/108/21/26/808 | 129/124/34/43/672 | 135/133/16/19/1256 | 114/108/22/28/865 | 136/131/33/40/759 | 136/133/17/21/1167 |
| 2 | 107/100/18/28/800 | 143/136/33/42/789 | 113/112/14/20/1130 | 108/102/21/28/780 | 142/137/36/43/730 | 135/132/18/22/1110 |
| 4 | 110/103/21/28/800 | 131/124/35/43/682 | 131/129/17/20/1167 | 106/100/21/27/817 | 135/128/34/43/723 | 116/113/20/24/850 |
| 9 | 118/110/22/30/859 | - | 134/132/16/19/1265 | 104/96/21/27/789 | - | 133/130/18/21/1158 |

^a Propellants all contain 88 wt% solids.

^b These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XIV

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 77°F AND 5% RELATIVE HUMIDITY IN STAGNANT NITROGEN ENVIRONMENT

| Time in Aging weeks | Mechanical Properties at 77°F, $\sigma/\sigma_0/\epsilon_0/\epsilon_0/E$ | | | | | |
|---------------------------|--|-------------------|---------------------------------|-------------------|-------------------|---------------------------------|
| | Unwrapped | | | Al Foil Wrapped | | |
| | Telagen S | | Minuteman | Telagen S | | Minuteman |
| | 66-954 | 67-98 | | 66-954 | 67-98 | |
| 0 | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b | 100/93/24/28/450 | 123/-/35/45/605 | 135/133/16/19/1250 ^b |
| 1 | 114/99/21/30/915 | 128/126/33/38/704 | 138/135/16/19/1459 | 118/100/22/32/852 | 129/124/33/40/732 | 129/128/19/19/1114 |
| 2 | 116/100/22/31/894 | 126/117/32/44/795 | 136/134/17/20/1156 | 109/106/19/24/784 | 124/121/27/33/688 | 136/134/15/18/1374 |
| 4 | 112/101/21/29/861 | 134/127/34/43/743 | 146/144/16/20/1374 | 111/94/22/31/808 | 126/121/33/42/686 | 141/139/17/19/1225 |
| 9 | 111/104/21/32/824 | - | 134/130/18/22/1112 | 112/107/21/30/824 | - | 127/125/16/19/1105 |

^aPropellants all contain 88 wt% solids.

^bThese values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XV

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 77°F AND 50% RELATIVE HUMIDITY IN STAGNANT NITROGEN ENVIRONMENT

| Time in Aging weeks | Mechanical Properties at 77°F, $\sigma_u/\sigma_b/\epsilon_u/\epsilon_b/E$ | | | | | |
|---------------------------|--|-------------------|---------------------------------|------------------|-------------------|---------------------------------|
| | Unwrapped | | | Al Foil Wrapped | | |
| | Telagen S | | Minuteman | Telagen S | | Minuteman |
| | 66-954 | 67-98 | | 66-954 | 67-98 | |
| 0 | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/19/19/1250 ^b | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/19/19/1250 ^b |
| 1 | 115/96/22/31/808 | 133/125/35/43/699 | 128/124/18/22/1101 | 114/98/22/30/822 | 124/116/30/42/798 | 141/139/16/19/1291 |
| 2 | 117/96/21/32/883 | 123/115/32/44/721 | 143/131/15/22/1549 | 115/98/21/30/861 | 121/113/30/42/769 | 138/131/16/19/1361 |
| 4 | 113/96/22/32/787 | 129/122/32/42/763 | 138/127/17/23/1254 | 110/90/21/32/835 | 129/120/32/44/743 | 133/116/17/25/1140 |
| 9 | 103/98/20/30/749 | - | 115/111/20/26/843 | 103/96/19/30/787 | - | 126/123/17/24/1077 |

^aPropellants all contain 88 wt% solids.

^bThese values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XVI
MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 77°F AND 25% RELATIVE HUMIDITY IN CIRCULATING AIR ENVIRONMENT

| Time in Aging weeks | Mechanical Properties at 77°F, $\sigma/\sigma_b/\epsilon_b/\epsilon$ | | | | | |
|---------------------------|--|-------------------|---------------------------------|-------------------|-------------------|---------------------------------|
| | Unwrapped | | | Al Foil Wrapped | | |
| | Telagen S | | Minuteman | Telagen S | | Minuteman |
| | 66-954 | 67-98 | | 66-954 | 67-98 | |
| 0 | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b |
| 1 | 118/99/21/30/933 | 130/124/33/42/743 | 124/121/19/23/1057 | 116/100/22/32/804 | 128/122/34/42/683 | 138/136/17/20/1250 |
| 2 | 118/100/23/33/789 | 127/118/32/43/839 | 140/137/19/22/1160 | 116/104/23/30/778 | 126/119/33/43/758 | 126/124/22/25/983 |
| 4 | 119/99/22/32/900 | 132/124/33/44/758 | 146/144/16/19/1402 | 115/96/22/32/856 | 129/121/33/44/756 | 146/143/16/20/1439 |
| 9 | 124/118/23/30/867 | - | 126/125/17/20/1099 | 114/109/21/30/850 | - | 118/115/20/23/922 |

^aPropellants all contain 88 wt% solids.

^bThese values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XVII
MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 77°F AND 50% RELATIVE HUMIDITY IN CIRCULATING AIR ENVIRONMENT

| Time in Aging weeks | Mechanical Properties at 77°F, $\sigma_u/\sigma_b/\sigma_c/E$ | | | | | |
|---------------------|---|-------------------|---------------------------------|------------------|-------------------|---------------------------------|
| | Unwrapped | | | Al Foil Wrapped | | |
| | Telagen S | | Minuteman | Telagen S | | Minuteman |
| | 66-954 | 67-98 | | 66-954 | 67-98 | |
| 0 | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b |
| 1 | 116/100/22/30/870 | 131/124/33/41/737 | 140/136/16/20/1413 | 112/98/21/30/878 | 124/114/31/43/759 | 142/140/17/20/1234 |
| 2 | - | 121/115/32/42/758 | 136/133/18/20/1232 | - | 124/116/32/43/719 | 133/130/18/21/1162 |
| 4 | - | 125/119/33/43/671 | 112/108/19/26/870 | - | 127/118/32/44/725 | 132/129/16/24/1143 |
| 9 | - | - | 116/113/19/22/1020 | - | - | 133/130/16/19/1241 |

^aPropellants all contain 88 wt% solids.

^bThese values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/125.

Table XVIII
MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 77°F AND 80% RELATIVE HUMIDITY IN STAGNANT AIR ENVIRONMENT

| Time in Aging weeks | Mechanical Properties at 77°F, $\sigma_u/\sigma_b/\epsilon_u/\epsilon_b/E$ | | | | | |
|---------------------------|--|-------------------|---------------------------------|------------------|-------------------|---------------------------------|
| | Unwrapped | | | Al Foil Wrapped | | |
| | Telagen S | | Minuteman | Telagen S | | Minuteman |
| | 66-954 | 67-98 | | 66-954 | 67-98 | |
| 0 | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b |
| 1 | 108/96/20/27/841 | 130/124/32/41/754 | 137/135/16/18/1280 | 115/94/22/32/804 | 129/123/32/40/759 | 145/143/16/19/1350 |
| 2 | 107/92/21/30/776 | 118/104/31/45/677 | 143/141/15/19/1501 | 109/90/22/32/787 | 120/104/33/47/649 | 138/136/17/20/1195 |
| 4 | 96/75/21/31/688 | 120/110/32/44/664 | 134/121/16/24/1350 | 94/76/22/32/594 | 121/110/30/43/730 | 128/116/16/23/1243 |
| 9 | 60/50/22/35/439 | - | 115/115/15/22/1025 | 67/57/22/34/468 | - | 112/109/16/23/931 |

^a Propellants all contain 88 wt% solids.

^b These values are values after aging at room temperature before storage begun. Properties after 12 day cure 20/-/34/45/425.

Table XIX
MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 170°F AND 25% RELATIVE HUMIDITY IN CIRCULATING AIR ENVIRONMENT

| Time in Aging weeks | Mechanical Properties at 77°F, $\sigma/\alpha/\epsilon_s/\epsilon_t/\epsilon$ | | | | | |
|---------------------------|---|------------------|---------------------------------|------------------|------------------|---------------------------------|
| | Unwrapped | | | Al Foil Wrapped | | |
| | Telagen S | | Minuteman | Telagen S | | Minuteman |
| | 66-954 | 67-98 | | 66-954 | 67-98 | |
| 0 | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b |
| 1 | 85/82/26/30/507 | 86/77/34/46/439 | 124/117/31/45/756 | 95/88/28/36/494 | 94/84/32/44/514 | 107/101/33/44/507 |
| 2 | 65/64/25/28/394 | 45/20/28/68/477 | 111/110/33/38/653 | 62/61/26/29/352 | 46/24/30/71/396 | 105/98/31/46/555 |
| 4 | 40/39/22/25/252 | 103/98/33/41/560 | 78/77/24/26/608 | 43/42/25/28/263 | 100/89/37/53/461 | - |
| 9 | 47/47/19/22/367 | - | 71/67/11/16/990 | 46/45/24/28/293 | - | 66/66/11/12/780 |

^a Propellants all contain 88 wt% solids.

^b These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XX
MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS^a
AT 170°F AND 80% RELATIVE HUMIDITY IN STAGNANT AIR ENVIRONMENT

| Time in Aging weeks | Mechanical Properties at 77°F, $\sigma_c/\sigma_u/\epsilon_u/\epsilon_s/E$ | | | | | |
|---------------------------|--|-----------------|---------------------------------|------------------|-----------------|---------------------------------|
| | Unwrapped | | | Al Foil Wrapped | | |
| | Telagen S | | Minuteman | Telagen S | | Minuteman |
| | 66-954 | 67-98 | | 66-954 | 67-98 | |
| 0 | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b | 100/93/24/28/650 | 123/-/35/45/605 | 135/133/16/19/1250 ^b |
| 1 | 48/48/21/21/289 | 54/51/31/38/343 | 104/90/24/39/577 | 69/66/27/32/365 | 56/48/34/48/323 | 120/110/27/42/699 |
| 2 | 21/20/26/28/102 | 27/21/30/41/214 | - | 52/50/26/30/302 | 35/23/32/56/311 | 93/87/32/46/413 |
| 4 | 22/22/27/30/97 | 30/28/24/28/195 | - | 36/35/25/28/196 | 48/47/30/34/294 | 70/69/18/49/570 |
| 9 | 25/24/22/25/136 | - | 41/40/5/5/920 | 29/28/23/26/175 | - | 43/43/6/6/822 |

^aPropellants all contain 88 wt% solids.

^bThese values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

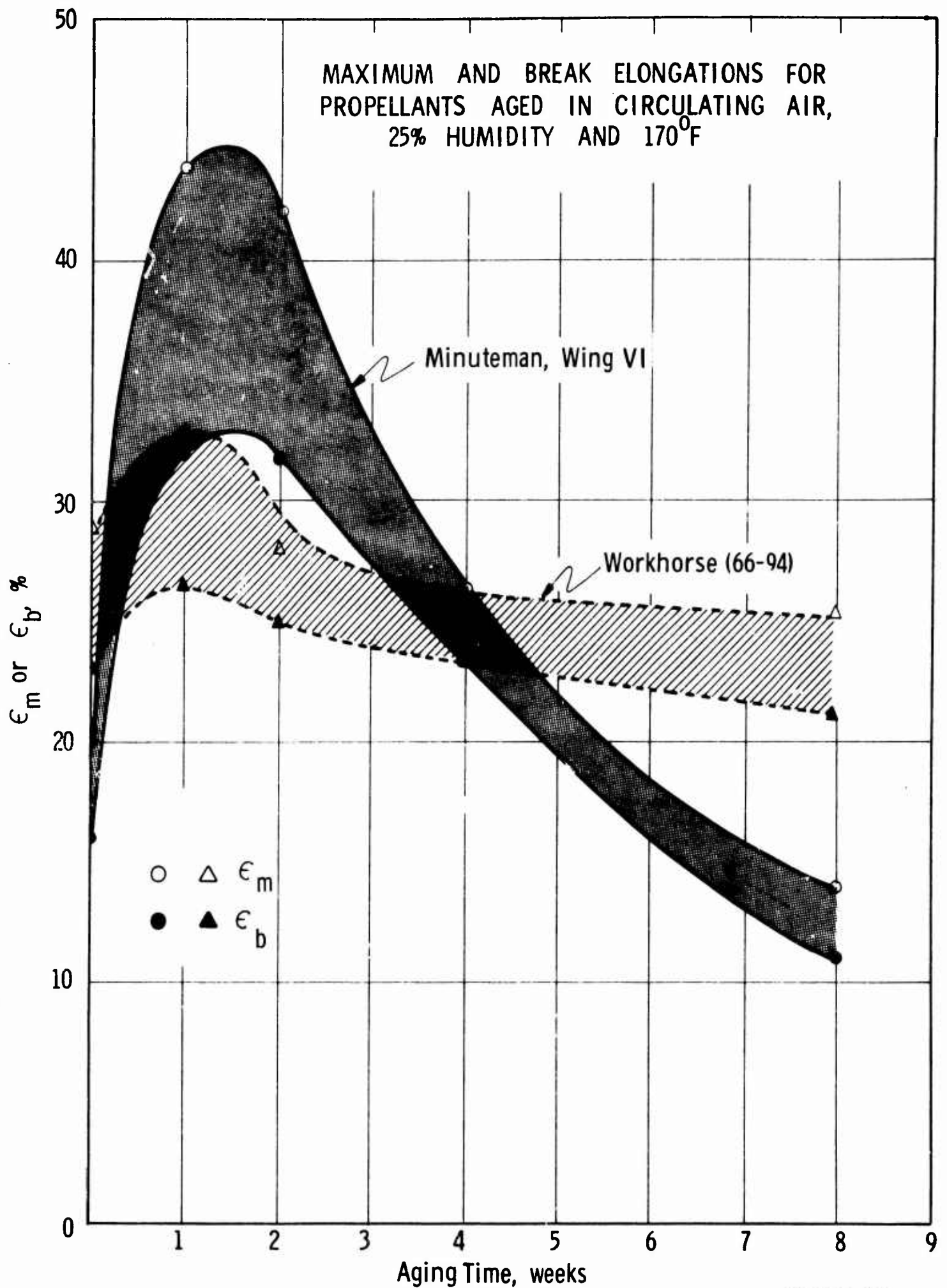
At 170°F both propellants have degraded rapidly. The Telagen S propellants rapidly lose tensile strength with little change of elongation. The unsaturated Minuteman propellant loses tensile strength while the elongation increases at first. The data at 9 weeks indicates that elongation of the unsaturated propellant decreases rapidly to very low values, probably because of oxidative crosslinking. There is some evidence that a recovery process may be occurring in the Telagen S propellant. This is best seen by comparing 4 week and 9 week data in Table XIX. The tensile strength and modulus have both increased. The same trend is seen in Table XX, but for these conditions (170°F and 80% relative humidity) the propellant has degraded far beyond usefulness. The effectiveness of the recovery process should be more clearly defined by 6 month data.

In general, there have been little differences between the aging behavior of wrapped and unwrapped samples. Only at 170°F and 80% relative humidity (Table XX) has there been a clear cut difference between the samples, the wrapped samples aging more slowly. At these conditions, however, the degradation was rapid for both the wrapped and unwrapped samples.

The aging data at 170°F is summarized in Figures 11-14.

c. Advanced Propellants

Telagen S propellants containing Be and LMH-2 were prepared and placed in aging in Phase Four of this program. After 6 months at 80°F and at 0 and 30% relative humidity, these propellants show no visual or hardness change. An LMH-1 Telagen S propellant was prepared as part of Task Four of Phase Five of this program and after 2 months at the above conditions, the propellant shows no visual or hardness change.



MAXIMUM AND BREAK ELONGATIONS FOR
PROPELLANTS AGED IN STAGNANT AIR,
80% HUMIDITY AND 170°F

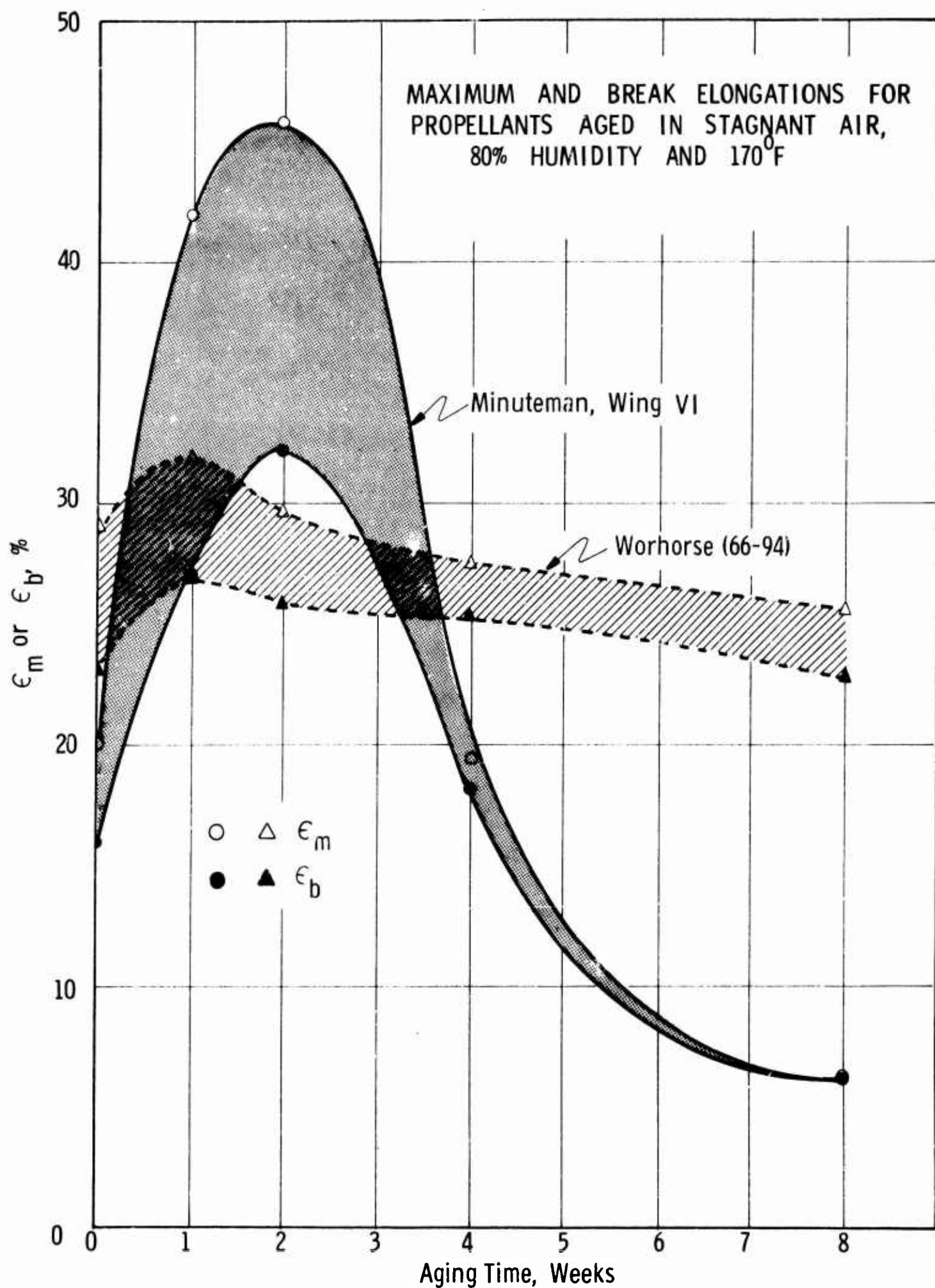


Figure 12

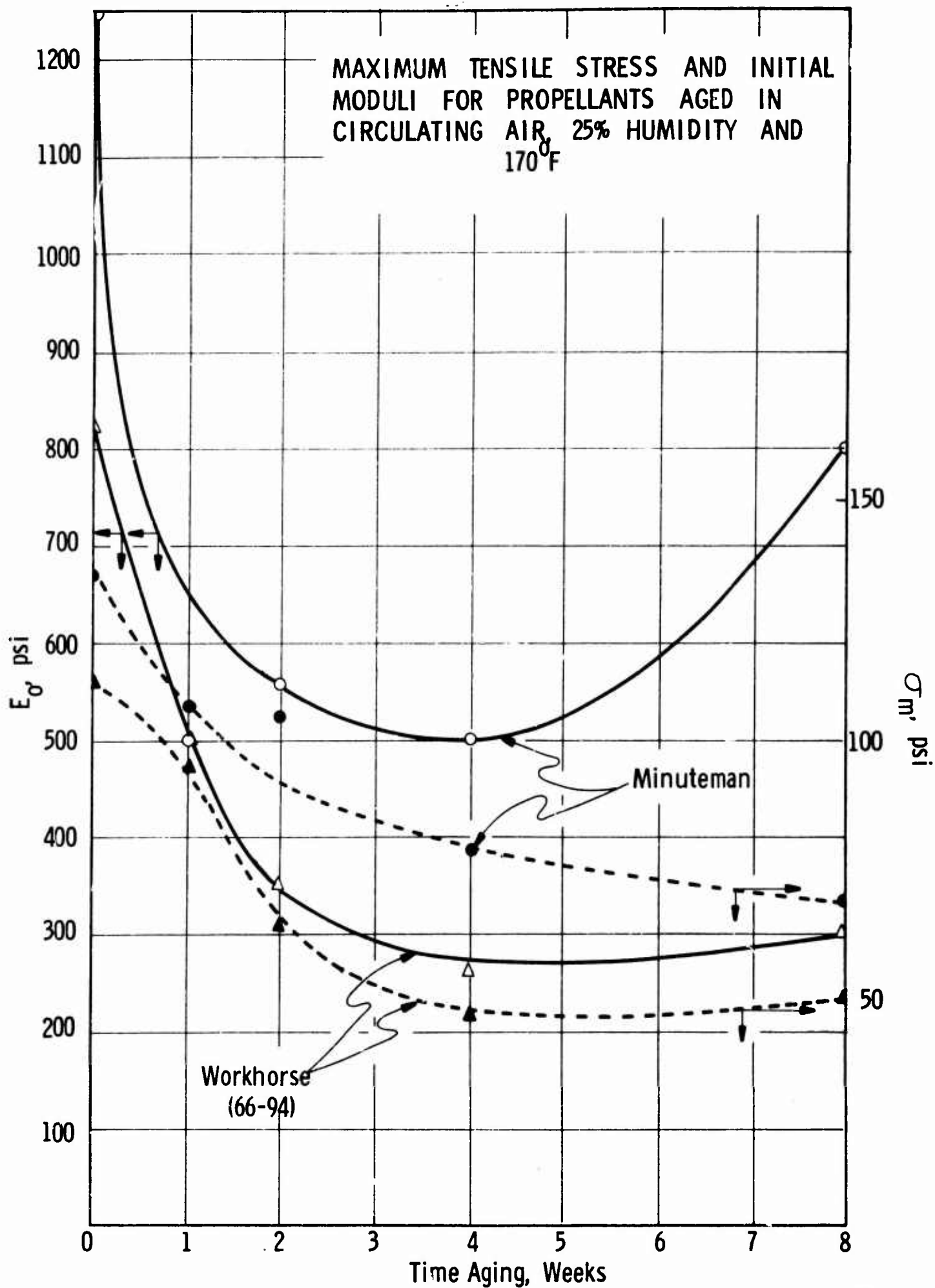


Figure 13

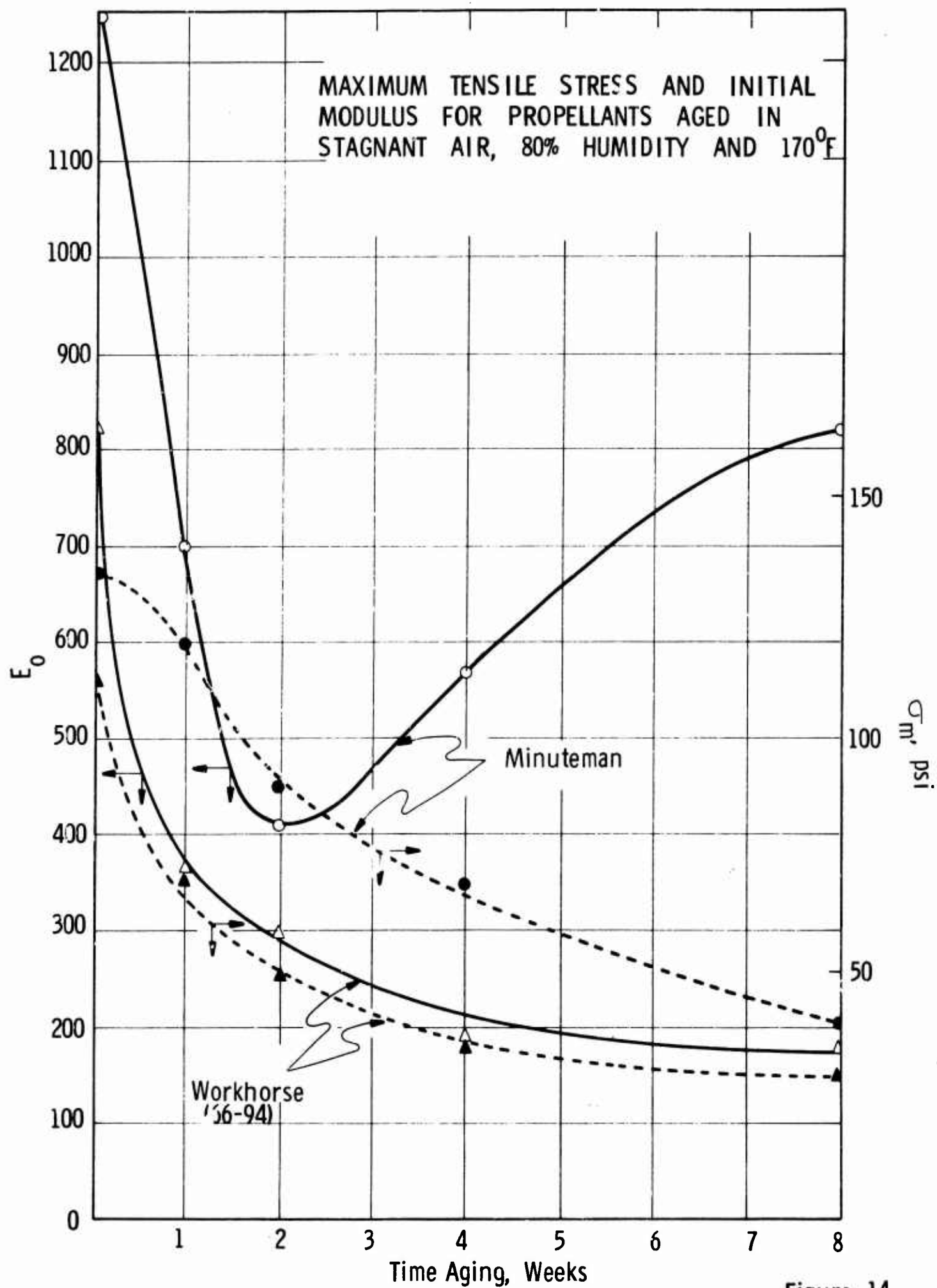


Figure 14

REFERENCES

- (1) B. E. Hudson and A. H. Muenker, "Functionality Determination of Binder Prepolymers", Esso Research and Engineering Company, Quarterly Progress Report 2, GR-2-FBP-67, 1 January to 31 March 1967. Contract FO4611-67-C-0012.
- (2) D. E. Johnson, R. H. Quacchia, and A. J. Di Milo, "The Development and Evaluation of a Hydrocarbon Binder for High Energy Solid Propellants" (U), Aerojet-General Corporation, Sacramento, California, AFRPL-TR-67-158, Contract AF 04(611)-11419, April 1967. (Confidential)
- (3) C. L. Robillard, Presentation at Conference on "Heat Sterilized Motor Technology", Second ICRPG/AIAA Solid Propulsion Conference, June 6-8, 1967, Anaheim, California.
- (4) D. E. Johnson and A. J. Di Milo, "The Development and Evaluation of a Hydrocarbon Binder for High Energy Solid Propellants" (U), Aerojet-General Corporation, Sacramento, California, AFRPL-TR-66-40, Contract AF 04(611)-10386, February 1966.
- (5) D. H. Wadsworth, J. Org. Chem., 32, 1184 (1967).

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

| | | | |
|---|---|---|--|
| 1. ORIGINATING ACTIVITY (Corporate author) Aerojet-General Corporation P. O. Box 15847 Sacramento, California | | 2a. REPORT SECURITY CLASSIFICATION None | |
| | | 2b. GROUP | |
| 3. REPORT TITLE THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS | | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Fifth Quarterly Report - 14 March - 13 June 1967 | | | |
| 5. AUTHOR(S) (Last name, first name, initial) Di Milo, Anthony J. Johnson, Duane E. Quaschia, Rodney H. | | | |
| 6. REPORT DATE July 1967 | 7a. TOTAL NO. OF PAGES 57 | 7b. NO. OF REFS 5 | |
| 8a. CONTRACT OR GRANT NO. AF 04(611)-11419 | 9a. ORIGINATOR'S REPORT NUMBER(S) 1030-81Q-5 | | |
| b. PROJECT NO. 3418 | 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) | | |
| c. | | | |
| d. | | | |
| 10. AVAILABILITY/LIMITATION NOTICES This document is subject to special export controls and each transmittal to foreign Governments or foreign nationals may be made only with prior approval of AFRPL (RPPR-STINFO), Edwards, California 93523 | | | |
| 11. SUPPLEMENTARY NOTES | | 12. SPONSORING MILITARY ACTIVITY Air Force Rocket Propulsion Laboratory Research and Technology Operations Edwards, California | |
| 13. ABSTRACT | | Air Force Systems Command United States Air Force | |
| <p>The acquisition and characterization of hydroxy terminated Telagen S was continued. The functionalities by molecular weight to equivalent weight ratio continue to be below 1.7, but cured binders indicated functionalities in excess of 1.85. The equivalent weights determined by reaction with n-butyl isocyanate were within 2% of values obtained by the manufacturer of the prepolymers. Thin-layer chromatography was used to demonstrate the presence of nonfunctional and monofunctional fractions in Telagen S. Considerable effort was devoted to improving the low temperature properties which may be caused by the high concentration of polar groups in the saturated binder. The use of substitutes for CTI and catalysts studies to achieve room temperature cures were also pursued. PAPI gave good cures with Telagen S, but 1,2,6-hexanetriol has been eliminated as a substitute for CTI. The processing of Telagen S propellants at room temperature is apparently limited more by prepolymer viscosity than by cure rate. Burning rate studies indicate very similar rates for saturated and unsaturated polybutadiene propellants. Cyclic imides have been eliminated as a cure system for advanced oxidizers because of very slow reaction rate with hydroxy groups. The more rapid reacting acid anhydrides have more potential in this area. After two months of aging at 170°F and at relative humidities in excess of 25%, both Telagen S and Minuteman Wing VI Second Stage propellants are degraded.</p> | | | |

DD FORM 1 JAN 64 1473

UNCLASSIFIED

Security Classification

UNCLASSIFIED
Security Classification

| 14 | KEY WORDS | LINK A | | LINK B | | LINK C | |
|----|---|--------|----|--------|----|--------|----|
| | | ROLE | WT | ROLE | WT | ROLE | WT |
| | Saturated Hydrocarbon Binders High Energy Solid Propellants Telogen S Burning Rate of Hydrocarbon Propellants Characterization of Saturated Prepolymers Thin-layer Chromatography Acid Anhydrides as Curing Agents Imides as Curing Agents Aging of Hydrocarbon Propellants | | | | | | |

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

UNCLASSIFIED
Security Classification